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<b>(21) International Application Number:</b> PCT/US97/15241 <b>(22) International Filing Date:</b> 29 August 1997 (29.08.97) <b>(30) Priority Data:</b> 60/024,976 30 August 1996 (30.08.96) US <b>(71) Applicant (for all designated States except US):</b> MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, Saint Louis, MO 63167 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KALOTA, Dennis, J. [US/US]; 1306 Green Mist Drive, Fenton, MO 63026 (US). CHOU, Yueting [US/US]; 315 Branchport Drive, Chesterfield, MO 63017 (US). HIRZEL, Timothy, K. [US/US]; 4614 Westminster Place, St. Louis, MO 63108 (US). SILVERMAN, David, C. [US/US]; 14314 Strawbridge Court, Chesterfield, MO 63017 (US). TOU, Jacob, S. [US/US]; 709 Winding Path, Ballwin, MO 63021 (US). CHO, Winsor, R. [US/US]; 718 Ridgewoods Manor Drive, Glencoe, MO 63038 (US). <b>(74) Agents:</b> SIECKMANN, Gordon, F.; Fitzpatrick, Cella, Harper & Scinto, 277 Park Avenue, New York, NY 10172 (US) et al.		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ZW. ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> NOVEL WATER SOLUBLE METAL WORKING FLUIDS  <b>(57) Abstract</b> <p>This invention relates to novel water soluble metal working fluid compositions, their use to work metal, a process for working metal using such compositions and the metal worked article of manufacture. More particularly, this invention relates to fluid compositions useful in cutting, grinding, shaping and other metal working operations which require a lubricant. The terms "first Group A" and "second Group B" are used herein to denote different groups and not to indicate any sequence of use or selection as any possible combination or sequence of use of a component(s) is envisioned without limit of any kind. The disclosed fluid compositions are also anticorrosive and environmentally more acceptable than current oil based fluids. There has now been discovered an essentially odorless, substantially non-oil misting, water-soluble metal working fluid comprising at least one component selected from a first Group A herein and optionally one or more components selected from a second Group B herein preferably with the balance of the composition being water and other (optional) minor ingredients. When a component is employed from Group A and a component is employed from Group B the action of the combination generally enhances performance of the resulting combination with contain moieties from both Group A and Group B.</p>		

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## NOVEL WATER SOLUBLE METAL WORKING FLUIDS

### BACKGROUND OF THE INVENTION

5 Metal working of a metal using a tool to work the metal is a practice which has been carried out for years. Prior art fluids have been used to facilitate such metal working. However, previously known oil-containing metal working fluids require reclaiming or disposal other than by discharging to common sewage treatment systems. In some cases the cost of disposal has become such a major cost that it approaches the  
10 initial cost of the fluid.

Without being bound by theory it is believed that metal working fluids fulfill one or more functions in various metal working applications. Typically, such illustrative nonlimiting functions include removal of heat from the work piece and tool (cooling), reduction of friction among chips, tool and work piece (lubrication), removal  
15 of metal debris produced by the work, reduction or inhibition of corrosion and prevention or reduction of build-up on edges as between the work piece and the tool. Thus these one or more functions usually require a formulation or combination of components in the lubricant fluid to accomplish the best attributes required for a particular metal working operation.

20 References for metal working disclaim an illustrative variety of metal working operations include The 12<sup>th</sup> American Machinist Inventory of Metalworking Equipment 1976-78, American Machinist, December 1978 and November 1983; McGraw-Hill, Inc. 1221 Avenue of the Americas, New York NY 10020;

Lubricants, Cutting Fluids, and Coolants; Wilbert J. Olds, Cahners Books, 89 Franklin Street, Boston, MA. 02110;

TRIBOLOGY IN METAL WORKING, Friction, Lubricant and Wear, John A. Schey, Professor, Department of Mechanical Engineering, University of Waterloo,  
5 Ontario, Canada, American Society for Metals, Metals Park, Ohio 44073. All three  
above references are incorporated herein in their entirety by reference.

Various fluids at times have been recently proposed to be substituted for oil-  
containing metal working fluids such as primary amides, ethylenediamine tetraacetic  
acid, fatty acid esters, and alkanolamine salts. Such compounds can be replenished  
10 during use by dissolving tablets containing such compounds during the useful life of  
the fluid. See U.S. Patent 4,144,188 to Sato.

Some amines have also been found useful in cutting oils as antibacterial agents.  
Such amines include alkanolamine and arylalkylamine such as p-benzylaminophenol.  
See EPO 90-400732 to Noda et al.

15 As noted above, one of the problems occurring in industry is the proper disposal  
of metal working fluids. The above mentioned amines are removed from the fluids by  
biodegradation, requiring facilities such as settling tanks, treatment tanks and sludge  
treatment tanks. Such a system is disclosed in Japanese Patent 03181395. Other  
methods of waste disposal and oil removal systems are employed to comply with  
20 environmental standards.

Worker safety can be an issue with presently employed oil-containing water  
soluble metal working fluids. Such fluids unavoidably come in contact with workers  
using the fluids in cutting, bending, threading and other metal working applications.  
Such oil-containing fluids may create a mist at the site of the work piece being operated



on or when the fluid is sprayed and such mist travels through the air in the vicinity of the machine and the operator thereof. Some attempts have been made to reduce the mist problem as is noted in British Patent 2,252,103. There is disclosed therein a polymeric thickener comprising a copolymer of acrylamide, sodium acrylate and N-n-octyl  
5 acrylamide. The copolymer is formulated with water soluble and water insoluble monomer.

Because of the misting and drift thereof in the work place employing some commonly employed water-soluble metal working fluids, there is usually associated with such work place a distinctive odor which permeates the entire area. Usually such  
10 odor is unpleasant and is tolerated as a condition which is unavoidable.

There is needed an odorless, non-oil misting, water soluble metal working fluid, particularly useful in cutting operations. There is also needed a fluid which would dispense with the need for disposal costs, and provide the work place with a more sanitary and acceptable atmosphere in which to work.

15

#### OBJECT(S) OF THE INVENTION

It is an object of the invention to provide an enhanced lubricating composition for use in metal working environments.

It is another object of the invention to provide an enhanced lubricating  
20 composition which is effective with and without use of a phosphate or phosphonate or borates.

It is a further object of the invention to provide an enhanced lubricating composition which is effective with the use of phosphorus containing compounds.

It is yet another object of the invention to provide an enhanced lubricating composition useful in extreme pressure applications.

It is yet a further object of the invention to provide an enhanced lubricating composition containing a lubricating imparting component which contains a carboxylate moiety and a phosphorus moiety within the same molecule.

It is yet a further object of the invention to provide an enhanced lubricating composition which is effective when used with borate compounds.

It is yet a further object of the invention to provide an enhanced lubricating composition containing a lubricating imparting mixture in which one component contains an amide and the same or a second component contains a phosphorus moiety.

Yet another further object of this invention is to provide an enhanced lubricating composition containing manufactured and naturally occurring polymers such as proteins used with or without a phosphorus moiety or borate moiety to provide the extreme pressure lubrication and additionally simple or boundary lubrication.

These and other objects are met in the invention herein, a nonlimiting description of which follows hereinafter.

#### BRIEF DESCRIPTION OF THE INVENTION

There has now been discovered an essentially odorless, substantially non-oil misting, water soluble metal working fluid useful for a variety of metal working operations, including without limitation cutting, grinding, forming, and the like comprising at least one component selected from a first Group A herein and optionally one or more components selected from a second Group B herein-- preferably with the balance of the composition being water and other (optional) minor ingredients. When a component is employed from Group A and a component is employed from Group B the

action of the combination generally enhances performance of the resulting combination. If desired optionally more than one component can be utilized from Group A and/or Group B depending on the specific application or in addition if desired a component from Group A can be an adduct of components from Group A and Group B whereby  
5 that resulting adduct component imparting enhanced lubrication contains a carboxylate and phosphorus moiety within the same molecule.

The invention comprises a method of metal working which comprises providing as a lubricant to said metal, a lubricating effective amount of a fluid lubricant  
10 composition comprising one or more water soluble components selected from: a first group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; a monocarboxylic acid(s) having one to six carbon atoms functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$   
15 alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters; sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide or polysulfide; mercaptocarboxylic acids, salts and esters; keto acids; amine  
20 substituted organo acids; substituted amino acids, salts and esters; organosulfonates; sodium or potassium sulfide, sodium or potassium hydrogen sulfide, organic acids containing one or more moieties selected from carboxylate, sulfate, sulfonate, phosphate, or phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from carboxylate, sulfate, sulfonate,

phosphate, or phosphonate present as the free acids or their salts, and additionally a moiety selected from sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; alone or optionally with one or more components selected from a second Group (B) comprising:

5

phosphates, borates, phosphonates, phosphites and hypophosphites; and

which composition provides a synergistic lubricating or added functionality effect when used with one or more component(s) of Group (A) and Group (B).

10

In one embodiment, the composition comprises a reaction product(s) of said composition associated with a component or components therein or the application of said composition to a metal being worked. The lubricants employed herein have a lubricant property selected from the group consisting of extreme pressure, boundary  
15 lubricant, simple film or anti-wear or combinations thereof. It is most preferred to employ a phosphate as a component of Group B of this invention along with polyamino acid or polycarboxylate or amide or polyamide or amino acid as a component of Group A.

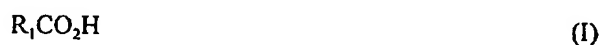
#### BRIEF DESCRIPTION OF THE DRAWINGS

20 Figures 1-18 are plots illustrating the metal working performance of compositions of this invention in various laboratory tests.

#### DETAILED DESCRIPTION OF THE INVENTION

Suitable components of Group A include, but are not limited to, carboxylic acids such as monocarboxylic acids having one to six carbon atoms functionalized or

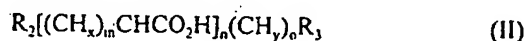
nonfunctionalized, examples are C<sub>1</sub> - C<sub>20</sub> alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; hydroxy carboxylic acid or a salt(s) thereof, and polycarboxylic acids, as the acids, partially neutralized acids or salts which carboxylic acids can be conveniently represented by the formulas



wherein connection with formula (I), R<sub>1</sub> is hydrogen, or C<sub>1-6</sub> alkyl, or R<sub>1</sub> is R<sub>a</sub>OR<sub>b</sub>, where R<sub>a</sub> is C<sub>6-20</sub> linear or branched alkyl, and R<sub>b</sub> is C<sub>1-6</sub> linear or branched alkylene, or

10 R<sub>1</sub> is

R<sub>c</sub>SR<sub>d</sub>, where R<sub>c</sub> is C<sub>1-20</sub> alkyl, and R<sub>d</sub> is C<sub>1-6</sub> alkylene or hydroxyalkylene with the proviso that these acids cannot be 2-hydroxybutyric or 3-hydroxybutyric acid, and wherein connection with formula (II),



15 R<sub>2</sub> and R<sub>3</sub> are selected as the same or different and may be independently hydrogen or oxygen, or an organic group including alkyl, aryl, mercapto, thio or dithioorganic moieties, hydroxy, hydroxyalkyl, alkenyl, alkoxy, alkoxyalkyl, or aromatic when employed in formula (II); y is numerically independent integer either 1 or 2; m is zero to about 40; o is about zero to about 18; and n is 1 to about 5,000 to 7,000 or more; m is zero to about 30  
20 and m, o and n are independent integers except that R<sub>1</sub> cannot be 3-carboxypropyl or a carboxymethyl substituted alkyl.

As employed herein, the term "alkyl" includes but is not limited to C<sub>1</sub> - C<sub>30</sub> alkyl, substituted and unsubstituted, linear and branched, functionalized and nonfunctionalized alkyls and includes also alkyl ethers and alkyl polyethers, mixtures thereof and the like.

Those of skill in the art will recognize after reading this specification that alkyl chain lengths above 30 may be employed. As employed herein the term "aryl" includes, but is not limited to, phenyl, substituted phenyl, biphenyl(s) and diphenyl ether, mixtures thereof and the like. Subscripts such as m, n, o, x and y, are conveniently employed herein are  
5 integers and vary independently from formula to formula and within formulas. Structure formulas employed herein are used to illustrate the various components and are not meant to limit the invention.

Illustratively, non-limiting examples of carboxylic acids and salts useful herein include formic acid, dithiodipropionic acid, polyacrylic acid, thioglycolic acid, lactic acid,  
10 1, 2, 3, 4-butanetetracarboxylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, dodecanedioic acid, glycolic acid, glyoxylic acid, glyceric acid, propanetricarboxylic acid, tricarboxyhexane, tartaric acid, ricinoleic acid, lactic acid, 3-dodecyloxypropionic acid, 3-octyloxypropionic acid, phosphonobutanetricarboxylic acid, a salt(s) thereof, mixtures thereof and the like.

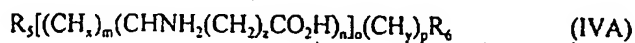
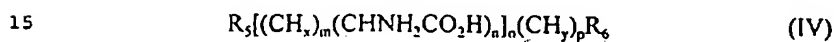
15 Other useful non-limiting carboxylic acid(s) include the group comprising of N-phosphonomethylglycine and water soluble salts and esters; lactic acid, formic acid, glycolic acid, glyoxylic acid, glyceric acid, octylthiobutyric acid, octylthiopropionic acid, octyloxypropionic acid, decyloxypropionic acid, dodecyloxypropionic acid, 4-methylthio-2-hydroxy-butyric acid, and salts and esters thereof and mixtures thereof and  
20 the like and is a polycarboxylic acid selected from the group consisting of polyacrylic acid, butanetetracarboxylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, dodecanedioic acid, undecanedioic acid, propanetricarboxylic acid, tartaric acid, sebacic acid, malic acid, fumaric acid,

citric acid, itaconic acid, citraconic acid, tartaric acid, malic acid, aconitic acid, and  
brassylic acid and tricarboxyhexane(s) and salts and esters thereof and the like.

Illustratively, non-limiting examples of salts of carboxylic acids useful herein  
include, but are not limited to, those such as the alkali metal, ammonium, and phosphonium  
5 salts, mixtures thereof and the like, including sodium, potassium and the like and mixtures  
thereof.

Also useful are carboxylic acid(s) containing two or more carboxylate moieties, if  
desired. The carboxylic acid may be a polymer with repeating units which has carboxylate  
groups.

10 Illustrative suitable amino acids useful herein as a component of Group A include,  
but are not limited, to both the naturally occurring amino acids and manufactured synthetic  
amino acid(s) containing at least one each of a carboxylic acid group and an amine group  
and which are conveniently represented by the formulas:



where  $R_4$ ,  $R_5$ , and  $R_6$  in formulas (III) and (IV) are either the same or different independently  
and may be independently hydrogen, alkyl or aryl; carboxyl; carboxymethyl; hydroxyalkyl; or  
amine; or sulfide; or mercaptan; phosphorus moieties;  $x$ ,  $y$ , and  $z$  as employed in these  
20 formulas (III) and (IV) are the same or different independently and either 1 or 2,  $m$ , and  $p$  as  
employed in these formulas are the same or different integers independently and are in the  
range from 0 to 6 and  $r$  is an integer varying independently from one to ten. However,  $n$  and  $o$   
must be at least one but can be integers from one to six independently, salts or esters thereof.

Typical useful non-limiting examples of suitable amino acids useful in practicing  
25 this invention include acidic amino acids, basic amino acids, neutral amino acids, and

mixtures thereof which are conveniently representative also of the immediately above described group.

Methionine hydroxy analog or a salt thereof is a useful amino acid herein.

Typical useful acceptable non-limiting acidic amino acids useful in practicing this invention include aspartic acid, including L-aspartic, D-aspartic and D,L-aspartic; and glutamic acid including L-glutamic, D-glutamic, D,L-glutamic; N-phosphonomethylglycine, its salt(s) and ester(s), N, N-di(2-carboxymethyl)-N-methylphosphonic acid mixtures thereof and the like.

Those of skill in the art will know that for purposes of metal working that the optical activity is not important meaning that the D, L, meso, racemic and other isomers function equally well.

Monocarboxylic acid(s) having one to six carbons functionalized or nonfunctionalized, examples are C<sub>1</sub> - C<sub>20</sub> alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid and hydroxy carboxylic acid(s) or a salt(s) thereof show extreme pressure lubrication.

Typical useful acceptable non-limiting examples of basic amino acids useful herein include arginine, histidine, tryptophan, ornithine, mixtures thereof and the like. Provided that when lysine, an amino acid, is employed as a component of Group A, then a borate may be employed as a component of Group B.

Illustrative useful non-limiting examples of acceptable sulfur containing amino acids of Group A which are useful herein in practicing this invention include cysteine, cystine, methionine, methionine hydroxy analog, homocysteine, felineine, isovalthine, penicillamine,



vitamin-U, (methyl methionine sulfone chloride) mixtures thereof, mixtures thereof, a salt(s) thereof and the like.

Other useful non-limiting amino acids which may be employed herein for illustration purposes include but are not limited to an amino acid or salt(s) thereof, a basic or a natural amino acid or a salt(s) or mixture of salt(s) thereof. Alanine, tyrosine, asparagine, valine, glutamine, glycine, hydroxyproline, isoleucine, leucine, phenylalanine, serine, threonine, thyroxine, phosphoserine, norleucine, norvaline, mixtures thereof, salts thereof and the like may be used herein.

Useful acidic amino acid(s) comprise aspartic acid and glutamic acid and isomers and racemic forms thereof and N, N-(2-carboxymethyl)N-methylphosphonic acid, N-phosphonomethylglycine, salt derivatives, and esters, O-phosphoserine and mixtures thereof.

Useful basic amino acid(s) comprise a basic amino acid selected from the group consisting of arginine, histidine, ornithine, and tryptophan and mixtures thereof and the like.

Illustratively, non-limiting useful amides of Group A which may be employed herein include those amides and polyamides which are water soluble as the compound or as its salt and where the nitrogen may be substituted or unsubstituted, and some of which are represented conveniently by the formula:

20



(V)

where  $R_7$ ,  $R_8$  and  $R_9$  as employed in formula (V) can be independently hydrogen, alkyl, aryl, a functionalized alkyl or functionalized aryl groups,  $\text{NH}_2$ ,  $\text{NHR}_{10}$ , or  $\text{NR}_{11}\text{R}_{12}$ , where  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  can be the same or different and are independently hydrogen, alkyl, functionalized alkyl, aryl, or functionalized aryl groups, are functional groups containing alkylaryl groups with the provision that  $R_8$  and  $R_9$  may not be polyethyleneimine, wherein when  $R_7$  is

MOOC(CH<sub>2</sub>)<sub>8</sub>, R<sub>8</sub> and R<sub>9</sub> may not be C<sub>1-4</sub> hydroxyalkyl and when R<sub>7</sub> is C<sub>12-18</sub> alkyl, R<sub>8</sub> and R<sub>9</sub> may not be hydroxyethyl-. Furthermore, if one of R<sub>8</sub> and R<sub>9</sub> is H, and the other is C<sub>3-30</sub> alkyl, then C<sub>7</sub> may not be selected from -CH<sub>2</sub>CH<sub>2</sub>COOH, -CH=CHCOOH, or ortho-carboxyphenyl. When one of R<sub>8</sub> or R<sub>9</sub> is H, and the other is CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)COOH, then R<sub>7</sub> may not be an alkyl group containing from 8 to 22 carbon atoms. The polyamides include both molecules containing two or more amide groups and polymers in which amide moieties are contained in the repeating units wherein M as used above, varies independently from formula to formula throughout this specification, but is defined such as in Formula XI, page 15.

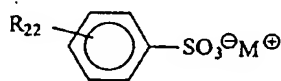
10 Non-limiting useful examples "functionalized alkyl" include 4-carboxybutyl, 4-butyl-1-sulfonic acid, 4-phosphonobutyl aspartyl, mixtures thereof and the like.

Non-limiting examples of useful acceptable amides for practicing this invention include but are not limited to asparagine, maleamic acid, urea, biuret, polyasparagine, guanidine, glutamine, polyurea, poly(2-ethyl-2-oxazoline), N, N-dimethylacetamide, 15 oleamide, polyvinylpyrrolidone, pyroglutamic acid, polyacrylamide, polylactams, N-cocoylglutamate, nonylamidoadipic acid, 4-nonylamidobutylsulfonic acid or a salt(s), mixtures thereof and the like.

As employed herein, the term amide and polyamides includes, but is not limited to those amides and polyamides which may be salts of a molecule containing an amide or a 20 polyamide or a mixtures thereof and esters of the molecule and partial salts as well. Non-limiting, illustrative examples are polyacrylamides, polyoxazoline(s) and maleamic acid which may be employed as a component from Group A. Without being bound by theory, it is believed that pre-cursors such as mono and diammonium maleate may be converted to maleamic acid at working temperature.

Illustratively, naturally occurring sulfur compounds of Group A useful herein include those such as the amino acids cystine, cysteine, methionine, homocysteine, feline, penicillamine, isovalthine, vitamin-U and manufactured products and mercaptocarboxylic acids such as mercaptosuccinic acid, dimercaptosuccinic acid, 2-mercaptopropionic acid, and mercaptoacetic acid, and the like are soluble in water as either the compound or its salt are useful in practicing this invention.

Non-limiting, illustrative examples of organosulfonates of Group A useful herein include the salts of alkylbenzene sulfonates and where the alkyl and/or the phenyl ring may or may not be substituted with functional groups such as



10

(VII)

where R<sub>22</sub> in formula (VII) may be independently alkyl substituted alkyl, alkoxy, hydrogen, aryl, aminoalkyl, amine, carboxyl, hydroxyl, or amide and M is independently hydrogen, alkali metal(s), ammonium, and organoammonium and mixtures thereof a salt(s) thereof, and the like.

Examples of useful non-limiting organosulfonates useful for practicing this invention include the alkali metal or ammonium salts of 4-octylbenzenesulfonic acid, 2-octylbenzenesulfonic acid, 3-octylbenzenesulfonic acid, 4-nonylbenzenesulfonic acid, 2-nonylbenzenesulfonic acid, 3-nonylbenzenesulfonic acid, 4-decylbenzenesulfonic acid, 2-decylbenzenesulfonic acid, 3-decylbenzenesulfonic acid, 4-undecylbenzenesulfonic acid, 2-undecylbenzenesulfonic acid, 3-undecylbenzenesulfonic acid, 4-dodecylbenzenesulfonic

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acid, 2-dodecylbenzenesulfonic acid, 3-dodecylbenzenesulfonic acid, and similar compounds containing different alkyl chain lengths, mixtures thereof and the like.

If desired, sodium or potassium sulfide or sodium or potassium hydrogen sulfide, or a mixture thereof may be employed as a component of Group A in practicing this invention.

5 Other useful illustrative components of Group A include but are not limited to manufactured and naturally occurring animal and vegetable derived protein mass such as glues derived from animals and albumins such as serum albumin (from blood), ovalbumin (from egg whites), lactalbumin (from milk), bovine serum albumin (BSA), insulin, somatotropin (bST), 1,2-Dithia-5,8,11,14,17,20,23,26-octathion, and other proteins, globulins such as those derived from animal serums, and casein. Further examples include collagen of skin, proteins derived from tendons and bones, elastin from arteries, and keratin of hair, nails and horns. Other examples of proteins include the glycoproteins, phosphoproteins and chromoproteins, mixtures thereof, a salt(s) thereof and the like.

15 Illustrative examples of proteins or polypeptides which are polyamino acids or salts or esters thereof useful herein as a component of Group A are polyamino acids which are those polyamino acids which include homopolymers of a single amino acid, block or random copolymers of a single or two or more amino acids mixtures thereof and the like, and including but not confined to natural or synthetic proteins, oligopeptides or polypeptides. Furthermore, the illustrative amino acids may be natural or synthetic, D- or L- or racemic forms available either through synthesis or from natural protein sources, both animal and vegetable, which are water soluble as either the free polymer or as a salt, and which are described conveniently by the following representative schematic formula:



where m as employed in this formula (VIII) is an integer varying independently from 1 to 12, n is an integer varying independently from about 2 to about 2000, such that the amino-

acid remains water soluble.  $R_{23}$  and  $R_{24}$  as employed in this formula (VIII) are the same or different and vary within one polymer chain and for example consist independently of hydrogen or  $-\text{CO}_2\text{H}$ ,  $-\text{CH}_2\text{CO}_2\text{H}$ ,  $-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ,  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ ,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $-\text{CH}(\text{CH}_3)_2$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ ,  $-(\text{CH}_2)_o\text{X}$  where  $o$  is 0 to 20 and  $X$  is any of

5  $R_{23}$ ,  $-\text{OH}$ ,  $-\text{SH}$ ,  $-\text{SSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ ,  $-\text{SCH}_3$ , phenyl, tolyl, hydroxyphenyl, guanidiny, pyrrolidiny,  $\text{NH}_2$ , imidazoyl, indolyl, acetoamido, mixtures thereof and the like. Non-limiting examples of useful suitable polyamino acids include polyglutamic acid, polyasparagine, polyaspartic acid and poly(aspartic/glutamic) copolymers, polyproline, or a copolymer of proline with another amino acid or a salt(s) thereof.

10 Illustrative, non-limiting sulfone acids may be employed as a component from Group A in this invention including those of the formula:



where  $R_{27}$  is selected from linear or branched, substituted or unsubstituted, alkyl, alkenyl, alkoxy, alkylamino groups having 6 to 20 carbon atoms optionally containing

15 one or more oxygen atoms, and  $R_{28}$  is absent or selected from linear or branched, unsubstituted or substituted alkylene or alkenylene, alkoxy, alkylamino groups containing 1 to 6 carbon atoms optionally containing one or more oxygen atoms and  $G$  is selected from  $-\text{CO}_2\text{M}$ ,  $-\text{OSO}_3\text{M}$ ,  $-\text{SO}_2\text{OM}$ ,  $-\text{OPO}(\text{OM})_2$ , or  $-\text{PO}(\text{OM})_2$  where  $M$  in connection herewith is  $\text{H}$ , alkali metal cation, alkaline earth metal cation,

20 ammonium.

Non-limiting examples of sulfone acids useful for practicing the invention as a component of Group A include the alkali metal or ammonium salts of octylsulfonylpropionic acid, dodecylsulfonylbutyric acid, dodecylsulfonylpropionic acid, N-octylsulfonyl-beta-alanine, nonylaminosulfonyl-propionic acid.

Illustrative, non-limiting keto acids of the formula



are useful herein as a component of Group A where  $R_{29}$  is selected from hydrogen, linear or branched, substituted or unsubstituted, alkyl, alkenyl, alkoxy groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and  $R_{30}$  is absent or selected from hydrogen, linear or branched, unsubstituted or substituted alkylene or alkenylene, alkoxy groups containing 1 to 6 carbon atoms optionally containing one or more oxygen atoms and G is selected from  $-CO_2M$ ,  $-OSO_2M$ ,  $-SO_2OM$ ,  $-OPO(OM)_2$ , or  $-PO(OM)_2$  where M is H, (hydrogen), alkali metal cation, alkaline earth metal cation, and organoammonium, ammonium, mixtures thereof and the like.

Non-limiting, illustrative examples of keto acids useful for practicing this invention include alkali metal or ammonium salts of octylsuccinate, decylsuccinate, dodecylsuccinate, and 5-oxo-hexadecanoic acid, mixtures thereof and the like.

Illustrative, non-limiting amine substituted organo acids of the formula

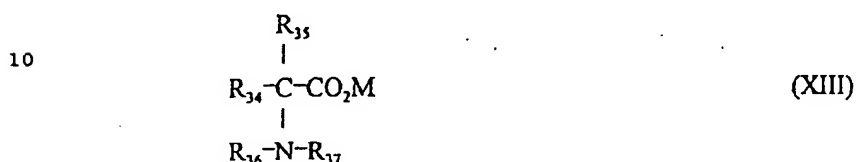


are useful herein as a component of Group A where  $R_{31}$  is selected from hydrogen, linear or branched, substituted or unsubstituted, alkyl, alkenyl, alkoxy groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and  $R_{32}$  is absent or selected from hydrogen, linear or branched, unsubstituted or substituted alkylene or alkenylene, alkoxy, and alkylamino groups containing 1 to 6 carbon atoms optionally containing one or more oxygen atoms and  $R_{33}$  is selected from II, linear or branched, substituted or unsubstituted alkyl or alkenyl groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and G is selected from  $-CO_2M$ ,  $-OSO_2M$ ,  $-SO_2OM$ ,  $-OPO(OM)_2$ , or  $-PO(OM)_2$  where M is H, alkali metal cation, alkaline

earth metal cation, organoammonium, ammonium mixtures thereof and the like with the proviso that when G in the compound above represented by the structure shown in formula (XII) is sulfonate,  $R_{31}$  and  $R_{33}$  are not hydrogen.

Non-limiting, illustrative examples of amine substituted organo acids of formula (XII) for practicing this invention include the alkali metal or ammonium salts of octylaminobismethylene phosphonic acid and dodecylaminobismethylene phosphonic acid.

Illustrative substituted amino acids of the formula:



are useful herein as a component of Group A wherein the compounds of formula (XIII) represent an extension of the amino acids wherein  $R_{34}$ ,  $R_{35}$ ,  $R_{36}$ , and  $R_{37}$  may be hydrogen, alkyl, aryl, functionalized alkyl, functionalized aryl, alkanol, polyalkoxy, alkenyl, sulfur containing moieties, and phosphorus containing moieties. Additionally,  $R_{34}$  and  $R_{36}$  may be covalently connected such as in cyclic amino acids like proline. M is a symbol for a moiety which is conveniently selected from hydrogen, alkali metals cation, ammonium, or organoammonium, mixtures thereof and the like.

Illustrative, non-limiting substituted acids of the formula



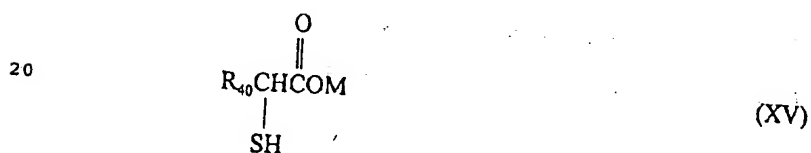
where  $R_{38}$  is selected from linear or branched, substituted or unsubstituted, alkyl or alkenyl groups having 6 to about 20 carbon atoms optionally containing one or more oxygen atoms, and X is absent or selected from the group consisting of  $-CH_2-$  (methylene), oxygen, sulfur,  $-S-S-$ , and aryl where aryl is unsubstituted or substituted

phenyl, and  $R_{39}$  is absent or selected from linear or branched, unsubstituted or substituted alkylene or alkenylene groups containing 1 to 6 carbon atoms optionally containing one or more oxygen atoms and G is selected from  $-\text{OSO}_3\text{M}$ ,  $-\text{SO}_2\text{OM}$ ,  $-\text{OPO}(\text{OM})_2$ , or  $-\text{PO}(\text{OM})_2$

5 where M is H, alkali metal cation, alkaline earth metal cation, ammonium with the proviso that:

1. when X is aryl and  $R_{35}$  is absent, G cannot be  $\text{SO}_2\text{OM}$  and
2. when X is absent or methylene, G cannot be  $\text{PO}(\text{OM})_2$  and
3. when G is a phosphate then  $R_{38}$  cannot be substituted with phosphate and
- 10 4. when X is absent or methylene or oxygen, G cannot be phosphate and
5. when G is phosphate  $R_{39}$  must be present and X cannot be methylene and
6. when G is  $-\text{SO}_2\text{OMg}$  and X is absent or methylene then  $R_{38}$ ,  $R_{39}$  cannot be alkyl or alkylene. (Mg = magnesium.)

15 Non-limiting, illustrative examples of mercaptocarboxylic acids useful as a component of Group A include without limitation those illustrated by the following schematic formula:



20 wherein  $R_{40}$  includes alkyl  $\text{C}_{1-30}$  and carboxyalkyl  $\text{C}_{1-30}$ , M = H, alkali metal cations, alkaline earth metal cation, ammonium, organoammonium, mixtures thereof, and the like.

25 Typical non-limiting, illustrative component(s) from Group B include any phosphates, phosphonates, phosphites and hypophosphites, borates, mixtures thereof, and



the like. When employed in the compositions, method of use and processes of this invention these phosphates, phosphonates, phosphites, hypophosphites, orthoborates, metaborates, pentaborates, can have beneficial effects on extreme pressure lubrication in metal working operations. Reduced forms of a component or components from Group B  
5 may be useful as such and also may be oxidized in-situ by air or other oxidizing agent. For example, phosphites may be oxidized to phosphates. Such beneficial effects are enhanced by the addition of these components to the organic compounds of Group A described herein above.

Non-limiting, illustrative most preferred phosphates are orthophosphates such as  
10 either the monobasic, dibasic or tribasic salt or mixtures thereof with an alkali metal(s), preferably a potassium or sodium, or an ammonium or alkylammonium such as triethylammonium or triethanolammonium and the like, and their full or partial esters although other similar phosphates may be employed if desired.

In addition to the orthophosphates, illustratively the following phosphates, as  
15 their salts, illustratively may be used: pyrophosphoric acid, metaphosphoric acid, phosphorous acid, hypophosphorous acid, polyphosphoric acid, phosphoserine, mixtures thereof and the like.

Some or most of the phosphonates useful herein are illustratively those compounds which can be represented conveniently by the formula:



where n in formula (IX) above is an integer varying independently from 1 to about 5, and  $R_{25}$  in formula (IX) can be independently organic moiety(s) and phosphonoorganic moiety(s), or amine containing organic moiety(s) or mixtures thereof and the like and  $R_{26}$  is independently one or more hydrogen or an organic moiety(s) including alkyl, aryl,

polyalkylene glycols, polyethyleneglycols, polypropylene glycols, mixtures thereof, and the like.

Suitable non-limiting, illustrative examples of acceptable phosphonates which are useful herein include 1-hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylenephosphonic acid), dodecylamine bismethylenephosphonic acid, which can be made by reacting dodecylamine, formaldehyde, phosphorous acid and hydrogen chloride, (hexamethylenediaminetetra(methylenephosphonic) acid, diethylenetriaminepenta(methylenephosphonic acid), N-phosphonomethylglycine, 2-phosphono-1,2,4-butanetricarboxylic acid, hydroxyphosphonic acid, and mixtures thereof, mixtures thereof and the like.

In preparing compositions of this invention (for example metal working compositions), the amount of a component selected from Group A, for example, is generally in the range from about 0.1% to about 75% or more by weight of the total composition and most preferably in the range from about 0.25% to about 25% by weight or more for the total composition (although one of skill in the art will recognize after reading this specification that greater or lesser amounts or concentrations can be employed if desired to attain the desired beneficial lubricant effect.

For example, when a component is utilized from Group A and a component is utilized from Group B, the amount of a component utilized from Group B is for example in the range from about 0.1 to about 60% and is preferably in the range from about 0.25 to about 15% by weight (although greater or lesser amounts can be employed as would be recognized by one of skill after reading this specification including the Examples).

In another embodiment, a method of metal working is provided which comprises contacting or communicating with the surface of the metal being worked or the surface

of the tool with an aqueous solution of a fluid lubricant composition comprising a composition of this invention as herein described.

If desired optionally more than one component can be utilized from Group A and/or Group B depending on the specific application or in addition if desired a component from Group A can be an adduct of components from Group A and Group B whereby that resulting adduct component imparting enhanced lubricating property contains a carboxylate and a phosphorus moiety within the same molecule. See Table I.

When the component from Group A is used exclusively, the amount of such component so employed is an effective lubricating amount, typically in the range from about 0.1 to about 75% or more and preferably in the range from about 0.25% to about 25% although greater or lesser amounts may be employed as those of skill in the art will recognize as an effective amount after reading this specification.

The phosphonates illustrated above may be used as a component of Group A to achieve one or more of the objects of this invention. When a phosphonate is so employed the concentration of the phosphonate is preferably in the range from about 0.1% to about 75% or more and preferably in the range from about 0.10% to about 15% and most preferably in the range from about 0.10% to about 10% by weight although greater or lesser amounts may be employed.

This invention also comprises a method of feeding a metal working water-soluble lubricant composition to a metal needing and receptive to the same (capable of being worked) comprising preparing an aqueous solution of a metal working water soluble lubricant composition by optional dilution of a composition of an aqueous solution of a fluid lubricant composition which comprises one or more water soluble components selected from a first group (A) comprising amides; polyamides; polyamino acids, salts

and esters; polycarboxylic acids, salts or their esters; amino acids, salts and esters, sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide; mercaptocarboxylic acids; substituted amino acids; organosulfonates; sodium or potassium sulfide, sodium or potassium hydrogen sulfide, organic acids

5 containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate; and phosphonate present as the free acids or their salts; and additionally a moiety selected from the group consisting of sulfone,

10 sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising phosphates, borates, phosphonates, phosphites and hypophosphites, preferably with the balance being water and feeding the water soluble composition to the work portion of a metal by spraying or dripping said metal working

15 water soluble composition. Illustratively, in using this invention, a lubricated metal surface is provided wherein said surface of said metal being worked and/or the surface of the tool is lubricated with a composition of this invention. Illustratively, such lubrication is brought about by any convenient means such as dripping, wetting and otherwise similarly providing or feeding in some acceptable fashion a composition of this invention

20 to the surface of the metal being worked so it is utilized to produce a metal worked piece also in accordance with this invention.

The temperature at which composition of this invention may typically be applied is preferably a suitable temperature, for example, such as might be arrived at by those of skill in the art and illustratively, but non-limiting, may be in the range from about 32°F to

about 212°F or more or less as measured in the fluid. Those of skill in the art will recognize that the temperature in the zone of the metalworking and of the tool and the metal being worked will necessarily become significantly hotter during the metal working. If desired, a metal may be worked by a tool using a composition of this invention whereby the metal is cleaned first and then this invention practiced on the metal.

Those of skill in the art will recognize that various water soluble additives may be employed in compositions of this invention to enhance or contribute properties which enable broader functions with respect to the use of the compositions in metal working applications. The types of additives which are readily apparent to those skilled in the art include simple film forming lubricants and/or boundary lubricants, corrosion inhibitors, oxidation inhibitors, detergents and dispersants, viscosity index improvers, emulsion modifiers, antiwear and antifriction agents and foam depressors.

For example, additives may be employed to enhance boundary lubrication such as wear inhibitors, lubricity agents, friction modifiers and the like. Typical examples of such additives are metal dialkyl dithiophosphates, metal diaryl dithiophosphates, alkyl phosphates, tricresyl phosphate, 2-alkyl-4-mercapto-1,3,4-thiadiazole, metal dialkyl-dithiocarbamates, metal dialkyl phosphorodithioates wherein the metal is typically zinc, molybdenum, tungsten or other metals, phosphorized fats and olefins, sulfurized fats and olefins and paraffins, fatty acids, polyalkoxylated fatty acids, alkylene oxides, polyethylene oxides, polypropylene oxides, carboxylic acids and their salts, esters of fatty acids including partially hydrolyzed castor oil, organic molybdenum compounds, molybdenum disulfide, graphite and borate dispersions. Such boundary lubrication

additives are well known in the art. Other additives include detergents and dispersants which provide cleaning functions.

Although the fluid compositions of this invention function as corrosion inhibitors in a certain range of pH, corrosion inhibitors may be employed in compositions of this invention which will function in a pH range in which another ingredient may not function as a corrosion inhibitor. Suitable examples of corrosion inhibitors include polyamino acids and phosphonates such as  $C_{12}H_{25}N(CH_2PO_3H)_2$ . Typical examples of corrosion inhibitors known in the art are benzotriazole, tolyltriazole, other functionalized benzotriazoles, zinc chromate, dithiophosphates such as zinc dithiophosphate, metal sulfonates wherein the metal is an alkali metal, alkanolamines such as monoethanolamine and triethanolamine and substituted alkanolamines wherein the backbone of the alkyl group is substituted to provide various properties, alkyl amines such as hexylamine and trioctylamine, borate compounds such as sodium or potassium tetraborate or potassium pentaborate, and mixtures of borates with amines, carboxylic acids including polyaspartic acid at high pH (about 10 and above) and alkyl amino carboxylic acids particularly useful in hard water, sodium molybdate, boric acid esters such as monobenzyl borate and boric acid with various ethanolamines (also acting as a biostat), caprylic acid, nonanoic acid, benzoic acid, nitro derivatives of benzoic acid,  $\alpha,\omega$ - diacids such as sebacic acid, ammonium benzoate, mucic acid, hydroxybenzoic acid, sodium benzoate, triethanolamine salts of carboxylic acids with a carboxymethyl thio group such as 1-1-(carboxymethylthio)undecanoic acid triethanolamine salt. Other corrosion inhibitors include 1-methylimidazole, 1-(3-aminopropyl)imidazole, 1,2-dimethylimidazole, mixtures thereof and the like, amines and substituted amines such as 2,2'-ethylenedioxy-bis(ethylamine), tris(2-aminoethyl)amine, N,N,N',N'-tetrakis(2-

hydroxyethyl)ethylenediamine, and longer chain mono-, di-, and triamines such as 4-(aminomethyl)-1, 8-octanediamine, iminobispropylamine, bis-hexamethylene-triamine, trioctyl amine, and polyethyleneimine, mixtures thereof and the like. An additional class of inhibitors are biological buffers such as 3-[N,N-bis(2-hydroxyethyl(amino))-2-hydroxy-propanesulfonic acid. Additionally, basic amino acids such as lysine and ornithine could also be added to provide corrosion inhibition. Lysine and ornithine are non-toxic and biodegradable and readily absorbed by the environment. A more thorough review of corrosion inhibitors are provided by Aruna Bahadur in a publication entitled "Chromate Substitutes For Corrosion Inhibitors in Cooling Water Systems" appearing in

5

10 Corrosion Reviews, 11(1-2), pp. 105-122, 1993 which is incorporated herein by reference in its entirety.

These fluids may be employed in metal working processes for both ferrous and non-ferrous metals if desired. Tests with non-ferrous metals such as brass, copper, aluminum, and titanium indicate that the work piece remains relatively free of

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discoloring deposits. It has been observed that the aqueous solutions of the salts of polyaspartic acid are corrosion inhibitors for ferrous metals as indicated by U.S. Patent 4,971,724 to Kalota et al. Therefore, metals, particularly ferrous metals, are free of harmful deposits and are, in fact substantially protected from corrosion by the metal working fluids of this invention.

20 The water-based metal working fluid compositions of this invention are particularly advantageous in that there is little or no odor associated with their water solutions. Further, it has been observed that these fluids do not create a mist around the tool working area as is common with water-based oil containing fluids. Because of the lack of mist formation the work area is maintained virtually free of deflected fluid

leaving the machinery and worker substantially free of contamination by the metal working fluid. The cost advantages of such a fluid are obvious in alleviating environmental concerns resulting in alternative means of disposal.

The metal working fluids of this invention are useful in the various metal  
5 working applications such as were noted above with any number of types of metals. In particular they are useful in working ferrous metals such as iron, steel (carbon steel and low alloy carbon steel), and stainless steel and nickel-based alloys. Non-ferrous metals which can be worked with fluids of this invention are copper, brass, aluminum, magnesium, zirconium, and titanium. In addition, alloys or composites made from such  
10 materials as cobalt or nickel cemented tungsten carbide may also be worked or formed using components in this invention.  $C_{12}H_{25}N(CH_2PO_3H)_2$  (dodecylamine bismethylene phosphonic acid) may be conveniently utilized when working aluminum metal as a component of Group B. Also polyalkylene oxide derivatives of fatty acids such as ricinoleic acid may be utilized. Such metals are safely worked with lubricity supplied by  
15 the water based fluids of this invention.

A particularly important function of a metal working fluid of this invention in cutting operations is the function of cooling so as to maintain lower temperature of the tool as well as the work temperature. Such control aids in minimizing tool wear and distortion of the work piece. Another function of the metal working fluid of this  
20 invention is lubrication which may reduce friction as between the tool and chips produced during the cutting operation as well as reduction of the friction between the tool and the work piece. In cutting operations of various types there are typically produced chips of small pieces of metal which are advantageously carried away from the work piece as soon as possible so that they do not jam the cutting tool.



As used herein, "water soluble" also includes, but is not limited to, the condition in which a substance forms a homogeneous transparent solution in water. Useful components in compositions of this invention include those wherein the component of Group A alone or the combination of a component Group A and a component of Group B are water soluble.

As used herein, the term "metal working" is not limiting but includes illustratively without limiting such processes as cutting, grinding and forming processes and similar processes and the like. According to M. C. Shaw, "Principles of Abrasive Processing", Clarendon Press, Oxford, 1996, which is incorporated herein in its entirety by reference, which discloses some metalworking aspects, the field of grinding is divided into two regimes, "stock removal grinding" and "form and finish grinding". The first regime involves those processes in which the main objective is to remove unwanted material without regard for the quality of the resulting surface. The second regime involves those operations in which form and finish are a major concern and wheels must be periodically dressed to provide sharp cutting edges that are relatively free of adhering metal and wear flats. Our invention relates to all types of grinding and forming. Illustratively, some of the types of grinding are rough grinding, precision grinding, surface grinding, cylindrical grinding, centerless grinding, internal grinding, creep feed grinding and tool grinding and the like.

Some of the metal cutting or metal removal operations include illustratively, without limit, turning, milling, honing, drilling, sawing, reaming, broaching, tapping, planing, boring, threading and the like. Illustrative, non-limiting types of operations are presented in M. C. Shaw, "Metal Cutting Principles", Clarendon Press, Oxford, 1984

which is incorporated herein in its entirety by reference. Metal removal processes are considered a type of forming but involve forming by removal of metal.

Forming processes typically have to do with the shaping of metal without its removal. Some nonlimiting illustrative examples are coining, explosive tube forming, 5 cogging, roll forming, bar forging, tube rolling, bending, stamping, and drawing among others. Such processes typically require high pressures which are believed to induce plasticity into the metal at the point of "working" and are accompanied by increased temperatures. Without being bound by theory, it is believed that the extreme pressure portion of the package reacts chemically with the metal surface during either a 10 pretreatment of the surface or during the metal working operation. It is likewise further believed that lubrication occurs through the removal of the chemically reacted film through contact. It is also believed that the film is regenerated by further reaction. The technical reference J. P. Byers, "Metalworking Fluids", Marcel Decker, Inc., NY, 1994 is informative on this point and is incorporated herein in its entirety by reference.

15 Also as employed herein, the term "metal working" encompasses but is not limited to a process or processes using a tool performing the metal working to a piece and/or a piece itself being metal worked and receiving the actions of a tool.

As used herein, the term "polycarboxylic" includes carboxylic acids or salts or esters thereof containing two or more carboxylate moieties.

20 As employed herein, added functional effects, include but is not limited to, the combined extreme pressure lubricating effect of Group A and Group B components was greater than obtained from either component alone.

Those of skill in the art will recognize that cations such as sodium, potassium, ammonium, organoammonium and the like are employed in compositions and methods

of this invention (with various components of Group A and Group B) as counterion(s) of an anion(s) the latter of which might be responsible in some way for the enhanced property without being bound by theory. (Such as lubrication).

This invention also comprises of a method for metal working, wherein said  
5 method comprises providing as a lubricant to said metal, a lubricating effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid  
10 having one to six carbons functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid with the proviso that these acids cannot be 2-hydroxybutyric or 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and  
15 esters, sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide; and mercaptocarboxylic acids, salts and esters; amine substituted organic acids, salts and esters; substituted amino acids, salts or esters; organosulfonates; sodium or potassium sulfide, sodium or potassium hydrogen sulfide, organic acids containing one or more moieties selected from the Group consisting of  
20 carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate; and phosphonate present as the free acids or their salts; and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine,

ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising:

phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used in  
5 an admixture with one or more component(s) of Group (A) and Group (B).

This invention also comprises of feeding a metal working water-soluble lubricant composition to a metal useful to receive the same, comprising optionally diluting said metal working water soluble lubricant composition and feeding the optionally diluted or non-diluted water soluble composition to a portion of the metal by applying whereby  
10 said composition is effectively provided to said metal.

This invention also comprises of a method of using a metal working water soluble lubricant composition which comprises providing as a lubricant to said metal, a lubricating effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbon atoms functionalized or nonfunctionalized, examples are C<sub>1</sub>-C<sub>20</sub> alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters; sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide and 2 mercaptocarboxylic acid; keto acids, salts and esters; amine substituted organic acid(s) or a salt(s) thereof; organosulfonates; sodium or

potassium sulfide, sodium or potassium hydrogen sulfide, organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate present as the free acids or their salts, and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising:

phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used with one or more component(s) of Group (A) and Group (B).

This invention also comprises of a method for metal working, wherein said method comprises providing as a lubricant to said metal, a lubricating effective amount of a lubricant composition comprising of one or more water soluble components selected from: a first Group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbons functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters, sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide; and mercaptocarboxylic acids, keto acids, salts and esters;

amine substituted organic acid(s) or a salt(s) thereof; organosulfonates; sodium sulfide, sodium hydrogen sulfide, organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate; and phosphonate present as the free acids or their salts; and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising: phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used in an admixture with one or more component(s) of Group (A) and Group (B).

This invention also comprises a lubricated metal surface wherein said surface of said metal being worked has been contacted with a composition comprising an effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbon atoms functionalized or nonfunctionalized, examples are  $C_1$ - $C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters; sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide; organosulfonates; sodium sulfide, sodium hydrogen sulfide,

organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; keto acids, salts and esters; amine substituted organic acid(s) or a salt(s) thereof; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate; and phosphonate present as the free acids or their salts; and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising:

phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used in an admixture with one or more component(s) of Group (A) and Group (B) lubrication has been provided.

This invention also comprises a worked piece of metal or a piece of metal being worked, said working being or having been accomplished by having contacted or provided to said metal with an effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbons functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric

acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters; sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide and mercaptocarboxylic acids; salts and esters; substituted amino acids, salts or esters; organosulfonates; sodium or potassium sulfide, sodium or potassium hydrogen sulfide, keto acids, salts and esters; amine substituted organic acid(s) or a salt(s) thereof, organic acid(s) containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate present as the free acids or their salt, and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, carboxylic ester, ketone, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising: phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used in an admixture with one or more component(s) of Group (A) and Group (B) to produce said article of manufacture.

One of skill in the art will know how to make and use the compositions disclosed herein after receiving this specification. The composition of claim 1 wherein the component of Group A is a salt or mixtures thereof, or the component of Group B is a salt or mixtures thereof, or both components of Group A and Group B is a salt or a mixture thereof or neither component of Group A or Group B is a salt.



The 1,3,6-tricarboxyhexane was prepared by hydrolyzing tricyanohexane with potassium hydroxide in water. The tricyanohexane was obtained as a co-product from the electrohydrodimerization of acrylonitrile.

In preparing a composition of this invention one of skill in the art will typically add a component from Group A optionally to a component of Group B to form an admixture in a selected quantity of water. There is no preferred order with respect to mixing or order of addition. The temperature at which a composition may be prepared may be ambient and pressure normal atmospheric. Use of a water soluble component (s) is required.

Those of skill in the art will recognize that an effective quantity of a functional moiety component (lubricant) from Group A and optionally Group B are present in a composition of this invention in order to achieve the objects of this invention. This may be provided in acid, salt, ester or a mixture of forms, such as an ionic form (such as a salt(s)). The amount provided is such that a functional lubricating effective amount is provided in a composition, a method of use, or an article of manufacture prepared using the invention. Illustratively but not limiting, an effective amount of lubricant is that amount of lubricant which adequately lubricates the surface of the metal being worked or tool working the metal for example and achieves the objectives of a quality lubricant as would be recognized by those of skill in the art. When a component from Group A is employed without a component from Group B, those of skill in the art will recognize that an aqueous solution containing an effective lubricating amount of the component from Group A may be applied to the surface of the metal or tool being lubricated. This invention also comprises compositions where a component of Group B is used with a component from Group A. In those situations an effective lubricating amount of a

component from Group B is employed along with an effective amount of a component of Group A. Components illustrated in the EXAMPLES are available commercially except were noted.

### EXAMPLES

#### EXAMPLE 1

An Extreme-Pressure Four-Ball Test was conducted according to the procedure of ASTM D2783, "Standard Method for Measurement of Extreme-Pressure Properties of Lubricating Fluids (Four-Ball Method)" incorporated herein by reference in its entirety. This test is used to rank the relative load carrying properties of lubricating fluids under a constant set of conditions. In this test, one steel ball is rotated under load against three steel balls held stationary. The test lubricant covers the lower three balls. The load is increased on the rotating ball as the test progresses and scar diameter measurements on the balls are made for ten ascending loads below the weld-point. The data is reported in Table 1 below as load wear index (kgf), average scar diameter (mm), and weld point (kgf). The load wear index is calculated from the tabulation of scar diameter versus applied load. The corrected applied loads (compensating for Hertzian diameter) of the largest 10 loads immediately preceding the weld point are averaged. Since the scar diameters are always measured at the same applied loads, the index becomes a function of the fluid and metals. Since all tests are conducted with the same metal type the load wear index is used to rank the abilities of a series of lubricants to minimize wear.

Table 1 is a set of data which has been generated running the previous two tests and which reports data for the four ball extreme pressure test as Mean Hertz Load, Welding Load, Non-seizure Load and Scar Diameter for the extreme pressure Four-ball test and data is reported for coefficient of friction. Note that Max load and torque values were generated as a result of running ASTM method D2783.

These data indicate that compositions of this invention are highly useful in metal forming and metal working operations.

ASTM test D3233B, "Standard Test Methods for Measurement of Extreme Pressure Properties of Fluid Lubricants (Falex Pin and Vee Block Methods)" incorporated herein by reference in its entirety, was run at a fluid temperature of 49C at 290 rpm and a concentration by weight which provides 365 milliequivalents /L of the component shown below for most examples.

The test component was generally dissolved in a container to provide 365 milliequivalents/Liter in water with and without phosphate at a level of about 0.75% or about 1.5% as orthophosphate with the balance of the composition being water. These test materials were evaluated using the ASTM D2783 Extreme Pressure Four ball test and the ASTM D3233B Pin and Vee block test.

Classes of components useful in practicing this invention for metal working are contained in the following Table 1. (Except wherein indicated otherwise, when a salt was employed herein, the potassium salt was used. The pH was typically about 9.5 to 10).

In the interpretation of the results of ASTM D-2783, a weld point of 250 to 400 kg-f is considered to be high extreme pressure capability with a value of 315 being average for high extreme pressure fluids. Values of 500 kg-f and greater are considered higher than normally encountered high extreme pressure behavior. The maximum load of the test is 800 kg-f.

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.											
***ASTM D2783 4-ball Extreme Pressure Test***											
Compound	Compound meq./L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index		Welding <sup>1</sup> Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure			
			Kg	mm				Coefficient of friction	Max load <sup>2</sup> K lbs	torque Inch-lbs	
water		0	10.8	126	na	na	2.97				
water		0	12.2	126	na	na	2.79	0.25	0.605	7	
water		0.05	13.8	126	na	na	2.87				
water		0.4	24.41	200	na	na	1.75	0.23	2.549	131	
water		0.75	56.2	400	na	na	1.5				
water		0.75	56.4	400	na	na	1.79	0.19	2.5	112	
water		0.75	58.1	400	na	na	1.54	0.23	2.612	105	
water		1.5	63.3	400	na	na	1.45				
2.48% sodium formate	365	0	26.59	250	na	na	2.52				
2.48% sodium formate	365	0.75	61.54	400	na	na	1.47				
3.29% lactic acid	364	0	22.42	160	na	na	1.68				
3.29% lactic acid	364	0.75	76.43	500	na	na	1.86				
4.6% 4-hydroxybutyric acid	365	0	20.4	160	na	na	1.64	0.09	4.5	85	
4.6% 4-hydroxybutyric acid	365	0.75	63.3	400	na	na	1.49	0.1	4.418	102	

na= none achieved

Maximum loads <sup>1</sup> 800 Kg    <sup>2</sup> 4.5 K lbs.

K<sub>2</sub>HPO<sub>4</sub> = dipotassium orthophosphate

KPA = potassium salt of polyaspartic acid (or potassium polyaspartate)

na= none achieved

Maximum loads <sup>1</sup> 800 Kg <sup>2</sup> 4.5 K lbs.K<sub>2</sub>HPO<sub>4</sub> = dipotassium orthophosphate

KPA = potassium salt of polyaspartic acid (or potassium polyaspartate)

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.										
			***ASTM D2783 4-ball Extreme Pressure Test***							
Compound	Compound meq./L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure			
							Coefficient of friction	Max load <sup>2</sup> K lbs	torque inch-lbs	****Pin & Vee Block Test**
Compound	meq./L	wt% PO <sub>4</sub>	Kg	Kg	Kg	mm				
11.1% octanoic acid	771	0	23.62	126	24	1.62	0.06	3,709	48	
11.1% octanoic acid	771	0.75	70.73	400	na	1.25	0.05	4,356	45	
10.89% ricinoleic acid		0	32.8	126	50	2.05	0.16	3,099	45	
10.89% ricinoleic acid		0.75	48	250	32	1.24	0.05	3,815	43	
3.5% sodium polyglyoxylate	364	0	22.38	160	na	1.44				
3.5% sodium polyglyoxylate	364	0.75	59.37	400	na	1.52				
2.74% DL-tartaric acid	364	0	40.8	315	na	1.61	0.11	4.5	109	
2.74% DL-tartaric Acid	364	0.75	87.65	620	na	2.06	0.1	4.5	101	
2.47% malic acid	368	0	39.75	315	na	1.78	0.12	4.5	116	
2.47% malic acid	368	0.75	107.7	800	na	2.28	0.18	3.02	122	
2.34 wt% citric acid	365	0	40.17	315	na	1.58	0.14	3,578	107	
2.34 wt% citric acid	365	0.75	90.23	620	na	1.75	0.11	4.5	105	
1.64 wt% oxalic acid	364	0	25.4	200	na	1.69	0.12	4.5	115	
1.64 wt% oxalic acid	364	0.75	88.5	620	na	2.14	0.16	3,648	131	
2.15 wt% succinic acid	364	0	38.9	325	na	1.76	0.11	4.5	102	
2.15 wt% succinic acid	364	0.75	91.1	620	na	1.73	0.11	4.5	112	
2.65% 1,3,6-tricarboxyhexane	364	0	21.4	200	na	1.754	0.078	4.5	76	
2.65% 1,3,6-tricarboxyhexane	364	0.75	168.2	>800	na	1.744	0.09	4.15	81	

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.											
***ASTM D2783 4-ball Extreme Pressure Test***											
Compound	Compound meq/L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding <sup>1</sup> Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure				
							Coefficient of friction	Max load <sup>2</sup> K lbs	torque inch-lbs	****Pin & Vee Block Test**	
2.13%											
1,2,3,4-butanetetra-carboxylic	364	0	103.15	800	na	1.99					
2.13%											
1,2,3,4-butanetetra-carboxylic	364	0.75	117.78	800	na	1.86					
2.14%											
1,2,3,4-butanetetra-carboxylic	364	0	81.5	620	na	1.9	0.2	3.097	127		
0.43%											
1,2,3,4-butanetetra-carboxylic	73	0	16.2	160	na	2.18	0.02	4.5	15		
0.43%											
1,2,3,4-butanetetra-carboxylic	73	0.28	22.3	200	na	1.85	0.17	3.54	132		
7.58 wt% lysine borate	364	0	28.03	200	na	1.39	0.09	4.5	84		
7.58 wt% lysine borate	364	0.75	60.28	400	na	1.42	0.09	4.5	92		
2.625% polyacrylic acid	364	0	86.21	620	na	1.76					
2.625% polyacrylic acid	364	0.75	123.52	800	na	1.73					
sodium NTA, 3.35%	388	0	28.9	250	na	1.94					
sodium NTA, 3.35%	388	0.75	53.6	400	na	1.59					
3.28%											
2-phosphono-1,2,4-butanetric arboxylic acid	365	0	83.5	620	na	1.75	0.13	4.176	78		

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.										
			***ASTM D2783 4-ball Extreme Pressure Test***				ASTM 3233 Extreme Pressure			
Compound	Compound meq./L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	Coefficient of friction	****Pin & Vee Block Test****		
								Max load <sup>2</sup> K lbs	torque inch-lbs	
3.28% 2-phosphon-1,2,4-butanetricar boxylic acid	365	0.75	112.1	800	na	1.87	0.11	3.72		90
0.66% 2-phosphon-1,2,4-butanetricar boxylic acid	73	0	16.67	126	na	2.3	0.38	1.045		103
0.66% 2-phosphon-1,2,4-butanetricar boxylic acid	73	0.75	72.28	500	na	1.58	0.16	2.762		97
4.79% 6-aminocaproic acid	365	0	13.9	126	na	1.99	0.09	4.5		89
4.79% 6-aminocaproic acid	365	0.75	57.5	400	na	1.62	0.09	4.5		86
2.43% aspartic acid	365	0	23.6	200	na	1.85				
2.43% aspartic acid	365	0.05	28.6	250	na	1.99				
2.43% aspartic acid	365	0.75	82.8	620	na	2				
2.43% aspartic acid	365	1.5	109.2	800	na	1.93				
4.86% aspartic acid	730	0	30.2	250	na	1.93	0.15	2.821		99
4.85% aspartic acid	730	0.75	67.4	500	na	1.8	0.14	3.666		103
7.29% L-aspartic acid		0	29.6	250	na	1.99	0.16	2.426		86
9.72% L-aspartic acid		0	34.5	315	na	2.57	0.17	2.643		93
2.68% L-glutamic acid	364	0	30.96	250	na	1.95	0.16	1.949		71
2.68% L-glutamic acid	364	0.75	118.46	800	na	1.83	0.13	3.521		96
6.55% N-cocoylglutamate		0	27.07	126	40	1.31	0.12	2.8		55
6.55% N-cocoylglutamate		0.754	107.66	620	na	1.68	0.08	4.428		58
5.66% histidine	365	0	23.63	200	na	2.23	0.1	4.5		94

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.											
***ASTM D2783 4-ball Extreme Pressure Test***											
Compound	Compound meq./L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding <sup>1</sup> Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure				
							Coefficient of friction	Max load <sup>2</sup> K lbs	***Pin & Vee Block Test*** torque inch-lbs		
5.66% histidine	365	0.75	67.92	500	na	1.77	0.11	4.5	106		
5.76% arginine	331	0	16.9	160	na	2.28	0.1	3.2	72		
5.76% arginine	331	0.75	98.7	620	na	1.67	0.105	3.55	83		
6.15% ornithine hydrochloride	365	0	24.7	200	na	1.49	0.09	3.727	96		
6.15% ornithine hydrochloride	365	0.75	91.8	620	na	1.81	0.08	3.927	92		
6.03% phenylalanine	365	0	17.8	126	na	1.79	0.07	4.5	65		
6.03% phenylalanine	365	0.75	31.31	200	na	1.23	0.07	3.75	62		
4.81% L-asparagine	364	0	24.11	200	na	2.01					
4.81% L-asparagine	364	0.75	112.64	800	na	1.88					
5.33 wt% L-glutamine	364	0	24.2	200	na	2.1	0.15	2.207	78		
5.33 wt% L-glutamine	364	0.75	96.2	620	na	1.7	0.11	4.5	104		
3.838 wt% DL-serine	365	0	22.7	200	na	2.13	0.15	2.557	95		
3.838 wt% DL-serine	365	0.75	65.9	500	na	1.78	0.1	4.5	93		
2.68% glycine	357	0	17.5	200	na	2.6	0.27	0.3	27		
2.74% glycine	365	0.75	113.4	800	na	1.89	0.091	4.5	88		
5.51% polyglutamic acid, sodium	363	0		315	na	1.5					
5.51% polyglutamic acid, sodium	363	0.75	98.07	620	na	1.5					
6.15% potassium polyaspartate	401	0	34	250	na	1.51					
1% sodium polyaspartate	73	0.15	22.06	200	na	2.22	0.11	3.161	89		
2.5% sodium polyaspartate	182	0	22.94	200	na	1.87					



Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.																
			***ASTM D2783 4-ball Extreme Pressure Test***				ASTM 3233 Extreme Pressure									
			K <sub>2</sub> HPO <sub>4</sub> as		Load Wear Index		Welding <sup>1</sup> Load		Last Non-seizure Load		Scar diameter for last load before weld		****Pin & Vee Block Test***			
			Compound		Kg		Kg		Kg		mm		Coefficient of friction		Max load <sup>2</sup> torque	
			meq./L		wt% PO <sub>4</sub>		Kg		Kg		mm		K lbs		Inch-lbs	
2.5% sodium polyaspartate			182	0.375	55.2	400	na	na	1.72	0.1	3.693	91				
2.5% sodium polyaspartate			182	0.75	77.03	500	na	na	1.48							
2.5% sodium polyaspartate			182	1.5	87.93	500	na	na	1.32							
5% sodium polyaspartate			365	0	31.7	250	na	na	1.69							
5% sodium polyaspartate			365	0	41	315	na	na	1.68							
5% sodium polyaspartate			365	0	39.03	315	na	na	1.77	0.09	3.864	74				
5% sodium polyaspartate			365	0.75	98.85	620	na	na	1.65	0.1	4.044	82				
5% sodium polyaspartate			365	0.75	122.29	800	na	na	1.73	0.11	3.743	93				
5% sodium polyaspartate			365	0.75	119.2	800	na	na	1.79							
10% sodium polyaspartate			730	1.5	135.86	800	na	na	1.6	0.08	4.125	70				
polyasparagine, 4.16%			364	0	30.1	250	na	na	1.54							
polyasparagine, 4.16%			364	0.75	97.2	620	na	na	1.58							
5.59% potassium polyaspartate			365	0	50.9	400	na	na	1.79							

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water:										
***ASTM D2783 4-ball Extreme Pressure Test***										
Compound	Compound meq/L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure			
							Coefficient of friction	Max load <sup>2</sup> K lbs	torque Inch-lbs	****Pin & Vee Block Test**
5.59% potassium polyaspartate	365	0	52.22	400	na	1.86	0.19	2 434	73	
5.59% potassium polyaspartate	365	0.05	55.4	400	na	1.59				
5.59% potassium polyaspartate	365	0.75	124.1	800	na	1.75				
5.59% potassium polyaspartate	365	0.75	128.72	800	na	1.77				
5.59% potassium polyaspartate	365	1.5		>800	na	1.94	0.12	3 443	89	
5.59% potassium polyaspartate+ 1.86% 1-hydroxyethylidene-1,1-dipho sphonic acid (HEDP)	365	90 mM HEDP								
4.17% Bovine serum albumin	365	0	56.7	250	100	1.15	0.24	1 092	96	
4.17% Bovine serum albumin	365	0.75	103.1	620	na	1.58	0.22	1 151	78	
1% Bovine Serum Albumin		0.5	81.2	500	na	1.47	0.19	2 899	116	
4.20% bovine somatotropin		0	55	200	126	1	0.26	2 082	86	
4.20% bovine somatotropin		0.75	102.5	620	na	1.71	0.12	2 593	67	
4.17% Bovine serum albumin		0	56.7	250	100	1.15	0.24	1 092	96	
4.17% Bovine serum albumin		0.75	103.1	620	na	1.58	0.22	1 151	78	
urea, 2.19%	365	0	13.5	126	na	2.71				
urea, 2.19%	365	0.75	68.1	500	na	1.65				
2.96% urea	493	1.5	99.92	620	na	1.5	0.16	3 366	110	

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.											
				***ASTM D2783 4-ball Extreme Pressure Test***				ASTM 3233 Extreme Pressure			
				Load Wear Index		Welding <sup>1</sup> Load		Last Non-seizure Load		Scar diameter (for last load before weld)	
				Kg		Kg		Kg		mm	
				K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>							
				Compound meq./L							
										****Pin & Vee Block Test**	
										Coefficient of friction	
										Max load <sup>2</sup>	
										K lbs	
										inch-lbs	
										torque	
										0.12	
										0.1	
										0.1	
										0.09	
										0.23	
										0.13	
										4.5	
										</	

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.									
***ASTM D2783 4-ball Extreme Pressure Test***									
Compound	Compound meq/L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding <sup>1</sup> Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure		
							****Pin & Vee Block Test**	Coefficient of friction	torque Inch-lbs
							Max load <sup>2</sup> K lbs		
5.44% methionine	364	0.74	64.17	400	na	1.33	4,464	0.06	70
5.45% penicillamine	365	0	84	500	na	1.49	4.5	0.077	75
5.45% penicillamine	365	0.75	91.4	500	na	1.31	4.5	0.077	75
0.545% penicillamine	36.5	0	12.6	126	na	2.4	0.3	0.248	22
0.545% penicillamine	36.5	0.75	12.7	126	na	1.41	4.5	0.124	120
4.38% sodium sulfide	561	0	108.15	800	na	1.92	2,139	0.2	94
4.38% sodium sulfide	561	0.75	nd	>800	na	2	2,122	0.19	92
6.17% N-phosphonomethylglycine	365	0	66.3	500	na	1.85			
6.17% N-phosphonomethylglycine	365	0.75	84.1	620	na	2			

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.											
				***ASTM D2783 4-ball Extreme Pressure Test***				****Pin & Vee Block Test**			

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.									
***ASTM D2783 4-ball Extreme Pressure Test***									
Compound	Compound meq./L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure		
							Coefficient of friction	Max load <sup>2</sup> K lbs	torque inch-lbs
0.0573% sodium pyrophosphate	2.15	0.75	53.57	400	na	1.62	0.16	3.317	114
6.26% 1-hydroxyethylidene-1,1-dipho sphonic acid	304	0		>800	na	2.07			
6.26% 1-hydroxyethylidene-1,1-dipho sphonic acid	304	0.75		>800	na	2.02			
6.755 wt% O-phosphoserine	365	0	92.6	620	na	1.69	0.08	4.5	77
0.676 wt% O-phosphoserine	36.5	0	21.2	200	na	2	0.23	2.465	86
1.71% glycerol-2-phosphate, Na	79.2	0	28.4	250	na	1.86	0.21	2.576	108
1.71% glycerol-2-phosphate, Na	79.2	0.75	76.35	500	na	1.68	0.17	2.708	102
3.28% 1,3-dihydroxyacetone dimer	182 mM	0	19.53	160	na	2.47			
3.28% 1,3-dihydroxyacetone dimer	182 mM	0.75	71.46	500	na	1.59			
7.2% 2,4,6-trichlorophenol	364 mM	0	70.33	400	na	1.46	0.1	3.826	80
7.13% 2,4,6-trichlorophenol	361	0.75	88.97	500	na	1.4	0.17	2.291	88
1.26 wt% K2B10O16.8H2O	21.5 mmol/L	0	63.6	500	na	1.92	0.14	3.605	108
1.28 wt% K2B10O16.8H2O + 5.59 wt% KPA	21.5 / 365	0	90.1	620	na	2.05	0.09	4.5	91
3.63%		0	59.4	400	na	1.48	0.08	4.5	82

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.										
***ASTM D2783 4-ball Extreme Pressure Test***										
Compound	Compound meq/L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg.	Welding <sup>1</sup> Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure			
							****Pin & Vee Block Test**	Coefficient of friction	Max load <sup>2</sup> K lbs	Torque inch-lbs
Compound	Compound meq/L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg.	Welding <sup>1</sup> Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	****Pin & Vee Block Test**			
poly(2-ethyl-2-oxazoline) + 1.26% potassium pentaborate octahydrate										
2.68% L-glutamic + 1.26% potassium pentaborate octahydrate		0	84.5	620	na	1.93		0.1	4.5	94
2.43% L-aspartic acid + 1.26% potassium pentaborate octahydrate		0	83.4	620	na	1.96		0.12	3.629	94
2.34% citric acid + 1.26% potassium pentaborate octahydrate		0	104.5	800	na	2.36		0.11	3.564	93
2.47% malic acid + 1.262% potassium pentaborate octahydrate		0	84.8	620	na	2		0.14	3.664	109
2.19% urea + 1.26% potassium pentaborate octahydrate		0	48.3	400	na	1.74		0.13	4.241	111
0.49% boric acid + 5.59% KPA		0	73.3	500	na	1.7		0.1	3.943	89
0.49% boric acid	792/365	0	16.9	160	na	2.04		0.07	2.577	21
2.79% potassium polyaspartate + 1.22% polyacrylate	253/111	0	119	800	na	1.785		0.079	3.55	62
2.79% potassium polyaspartate + 1.22%	253/111	0.75	149.5	800	na	1.463		0.113	2.7	70

Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.										
			***ASTM D2783 4-ball Extreme Pressure Test***							
Compound	Compound meq./L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding <sup>1</sup> Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure			
							****Pin & Vee Block Test**	Coefficient of friction	Max load <sup>2</sup> K lbs	torque inch-lbs
polyacrylate, potassium salt	191	0	17	160	na	1.759		0.111	3	75
2.1% polyacrylate, potassium salt	191	0.75	162.7	800	na	1.978		0.154	2.5	89
0.41% polyacrylate, potassium salt	37	0	10.1	126	na	2.894		fail	fail	fail
0.41% polyacrylate, potassium salt	37	0.75	64.4	400	na	1.22		0.224	2.1	111
0.41% polyacrylate + 0.56% potassium polyaspartate	57/36.6	0.75	85	500	na	1.365		0.192	2	91
2.59% polyacrylamide	364	0	37.4	315	na	1.75		0.12	4.5	117
2.59% polyacrylamide	364	0.75	118.4	800	na	2.13		0.11	4.162	102
2.79% KPA + 1.3% polyacrylamide	182/183	0	53.1	400	na	1.62		0.08	4.242	82
2.79% KPA + 1.3% polyacrylamide	182/183	0.75	123.4	800	na	1.75		0.1	3.974	95
0.52% polyacrylamide	73	0	17.8	126	na	2.3		0.03	0.84	72
0.52% polyacrylamide	73	0.75	69.45	500	na	1.73		0.16	3.149	112
2.86% polyethyleneimine-80% ethoxylated		0	21.22	160	na	1.85		0.12	2.899	71
2.86% polyethyleneimine-80% ethoxylated		0.75	76.07	500	na	1.58		0.09	4.5	84
4.79% 6-aminocaproic acid		0.75	57.5	400	na	1.62		0.09	4.5	86



Table I cont'd

Four-ball extreme pressure and pin and vee block evaluation of several classes of compounds in water.											
***ASTM D2783 4-ball Extreme Pressure Test***											
Compound	Compound meq./L	K <sub>2</sub> HPO <sub>4</sub> as wt% PO <sub>4</sub>	Load Wear Index Kg	Welding Load Kg	Last Non-seizure Load Kg	Scar diameter for last load before weld mm	ASTM 3233 Extreme Pressure				
							Coefficient of friction	Max load <sup>2</sup> K lbs	torque inch-lbs		
5.48 wt% Mercaptosuccinic acid	365	0		>800	na	1.84	0.01	4.5	93		
5.48 wt% Mercaptosuccinic acid	365	0.75					0.09	4.5	90		
3.31 wt% Dimercaptosuccinic acid	365	0					0.11	4.431	118		
3.31 wt% Dimercaptosuccinic acid	365	0.75					0.23	2.196	116		
3.36 wt% Mercaptoacetic acid	365	0					0.09	4.5	88		
3.36 wt% Mercaptoacetic acid	365	0.75					0.11	3.655	89		
3.87 wt% 2-mercaptopropionic acid	365	0					0.1	4.172	85		
3.87 wt% 2-mercaptopropionic acid	365	0.75					0.1	3.215	73		
5.85 wt% (alpha) 2-hydroxyOctanoic acid	365	0					0.18	1.776	43		
5.85 wt% (alpha) 2-hydroxyOctanoic acid	365	0.75					0.16	3.528	45		
7.894 wt% 12-hydroxyDodecanoic acid	365	0					0.12	3.356	47		
7.891 wt% 12-hydroxyDodecanoic acid w/0.75% PO <sub>4</sub>	365	0.75					0.07	3.307	56		
3.8% dithiodipropionic acid	365	0	98.2	620	na	1.63	0.19	2.5	111		
3.8% dithiodipropionic acid	365	0.75	130.97	800	na	1.67	0.21	2.24	107		

Table I cont'd

[illegible]

### EXAMPLE 2

A series of experiments using the procedures of ASTM D2783 and ASTM 3233B were run to measure the extreme-pressure lubricating properties of compositions selected from several classes of compounds. The pH of the solutions were generally  
5 adjusted to about 10. The results are depicted in Figures 1 through 12. Figure 1 shows the scar diameter vs applied load for sodium polyglutamate in the presence and the absence of potassium orthophosphate. Figure 2 shows the scar diameter vs applied load for polyasparagine in the presence and absence of potassium orthophosphate. Figure 3 shows the scar diameter vs applied load for L-aspartic acid in the presence and absence of  
10 potassium orthophosphate. Figure 4 shows the scar diameter vs applied load for L-asparagine in the presence and absence of potassium orthophosphate. Figure 5 shows the scar diameter vs applied load for L-cystine in the presence and absence of potassium orthophosphate. Figure 6 shows the torque vs load for L-cystine and L-cysteine in the presence and absence of potassium orthophosphate. Figure 7 shows the scar diameter vs  
15 applied load for dithiodipropionic acid in the presence and absence of potassium orthophosphate. Figure 8 shows the scar diameter vs applied load for urea in the presence and absence of potassium orthophosphate. Figure 9 shows the scar diameter vs applied load for 1-hydroxyethylidene-1, 1-diphosphonic acid in the presence and absence of potassium orthophosphate. Figure 10 shows the scar diameter vs applied load for 2-  
20 phosphono-1,2,4- butanetricarboxylic acid in the presence and absence of potassium orthophosphate. Figure 11 shows the scar diameter vs applied load for sodium sulfide in the presence and absence of potassium orthophosphate. Figure 12 shows the scar diameter vs applied load for 2-phosphono-1,2,4-butanetricarboxylic acid (PBTC) in the presence and

absence of potassium orthophosphate. Figure 14 shows the scar diameter vs. applied load for Bovine serum albumin in the presence and absence of orthophosphate.

Figure 15 shows the scar diameter vs. applied load for poly(2-ethyl-2-oxazoline) in the presence and absence of phosphate. Figure 16 shows the scar diameter vs. applied load for malic acid in the presence and absence of phosphate. Figure 17 shows the scar diameter vs. applied load for tricarboxyhexane in the presence and absence of phosphate. Figure 18 shows the scar diameter vs. applied load for succinamic acid in the presence and absence of phosphate.

### EXAMPLE 3

10 The test solutions were prepared by dissolving the 1, 2, 3, 4-butanetetracarboxylic acid in water and adjusting the pH to 10. The solutions were tested using a Four-ball Extreme Pressure machine. The scar diameter and the applied load at which welding occurred were measured. Figure 13 below shows the results of the Four-ball extreme pressure test. The high pressure shows the independent lubricating properties  
15 of this molecule which can be employed with or without a component of Group B.

### EXAMPLE 4

Bovine somatotropin (bST) is an animal protein which can be employed in this invention as a component of Group A, for example. bST solution was tested by the ASTM D4172 "Wear Preventative Characteristic of Lubricating Fluids (Four-ball test) with  
20 both aluminum and steel balls. There was no noise during the tests for all three bST concentrations shown in Table II below. The scar diameter and friction coefficients indicate that the fluid has lubricant capability.

Table II

	4-ball on Aluminum	4-ball on Steel	Timken friction coef.
	Scar dia.mm	Scar dia.mm	Steel 2lb
bST 1.0%	0.81	0.56	0.16
bST 1.0%	0.72	0.55	Not Measured
bST 2.0%	0.50	0.55	0.17

5

Figure 14 below shows using ASTM method D2783 it was shown that a mixture of bST with phosphate afforded a synergistic extreme pressure lubricating effect affording a weldload at of 200 kg as bST alone and a weldload of 620 when bST and phosphates were together.

10

EXAMPLE 5

A solution of 7.5% bovine serum albumin (BSA) and 5.0% phosphate ( $\text{PO}_4^{3-}$ ) in water at pH 8.60, was diluted 9:1 with water, and run in the Timken tester using a steel ring and a carbon steel block, obtaining a friction coefficient of 0.20. (conditions: 2 lb normal force applied). The source of the bovine serum albumin employed was fraction V material, isolated by the heat-shock method (material obtained from Sigma Chemical Company).

15

Solutions of BSA in water were tested in the 4-Ball tester, using three fixed aluminum balls and one rotating steel ball. A 7.5% solution of BSA afforded a 0.7 mm scar diameter, making no noise during the test. A 0.75% solution of BSA afforded a 0.6 mm (mm=millimeter) scar diameter, also making no noise during the test. Using ASTM method D2783 it was shown that a mixture of BSA with phosphate afforded a synergistic extreme pressure lubricating effect affording a weld load of 250 kg without phosphate and a weld load and 620 kg when phosphate was added.

25

EXAMPLE 6

A solution of 1 wt% dodecylamino -N,N- bismethylenephosphonic acid in water, adjusted to a pH of about 6 was examined using the test method described in ASTM D4172, "Wear Preventative Characteristic of Lubricating Fluids (Four-Ball test)",  
5 incorporated herein by reference, with both aluminum and steel balls. The scar diameter on steel was 0.45 mm and on aluminum was 0.55 mm to both cases (see Table III below), there was no noise (sound from the test itself) during the test. These results indicate that the fluid has lubricant capability. This is an example of a component of Group A being employed exclusively, that is without a component from Group B in  
10 practicing this invention.

EXAMPLE 7

A solution of 1 wt% octylsulfonylbutyric acid in water, adjusted to a pH of about 9 was examined using the test method described in ASTM D4172, "Wear Preventative Characteristic of Lubricating Fluids (Four-Ball test)", incorporated herein by reference,  
15 with 6061 aluminum balls. The scar diameter on aluminum was 0.49 mm (see Table III below), there was no noise during the test. This solution was further examined using a method involving drilling 20 1/4" holes into a 356 aluminum block. No noise was produced in the drilling process and no oversized hole was found. These results indicate that the fluid has lubricant capability. This is an example of a component of  
20 Group A being employed exclusively, that is without a component from Group B in practicing this invention.

Table III: Examples of Group A Being Employed Exclusively

No.	Compound Name	Compound Formula	AL 4-Ball 1% scar dia.	AL 4-Ball 1% noise	AJ Drill no. of holes without noise
1	octylthiobutyric acid	$C_8-S-C_3CO_2H$	0.48	No	20
2	octylthiopropionic acid	$C_8-S-C_2CO_2H$	0.6	No	NT
3	octylsulfonylbutyric acid	$C_8-SO_2-C_3CO_2H$	0.49	No	19-20
4	(octyl/decyl)oxy-propanoic acid	$(C_8/C_{10})-O-C_2CO_2H$	0.4	No	20
5	dodecyloxy-propionic acid	$C_{12}-O-C_2CO_2H$	0.4	No	20
6	monooctyl succinate	$C_8-OC(O)C_2CO_2H$	0.53	No	NT
7	N-octylsulfonyl Beta-alanine	$C_8-SO_2NHC_2CO_2H$	0.98	Slight	NT
8	nonylamino sulfonylpropanoic acid	$C_9-NHSO_2C_2CO_2H$	0.5	No	NT
9	nonylamido adipic acid	$C_9-NHCOC_4COOH$	0.45	No	18-20
10	N-cocoyl glycine	$C_{11}(blend)-CONHCH_2CO_2H$	0.45	No	NT
11	dodecyltriethoxy sulfate	$C_{12}O(EtO)_3-OSO_2OH$	0.72	No	NT
12	dodecyltetraethoxy sulfate	$C_{12}O(EtO)_4-OSO_2OH$	0.74	No	NT
13	dodecylaminobismethylenephosphonic acid	$C_{12}-N(CH_2PO(OH)_2)_2$	0.55	No	20
14	octylaminobismethylenephosphonic acid	$C_8-N(CH_2PO(OH)_2)_2$	0.78	No	NT
15	4-methylthio-2-hydroxybutyric acid	$MeSC_3CH(OH)CO_2H$	0.8	No	NT
16	dodecylphenylsulfonic acid	$C_{12}-Ar-SO_3H$	0.53	No	NT

No	Compound Name	Compound Formula	AL 4-Ball 1% scar dia.	AL 4-Ball 1% noise	Al Drill no. of holes without noise
Comparative Examples:					
1	N-lauroylsarcosine acid	$C_{11}-CON(CH_3)CH_2CO_2H$	0.48	No	NT
2	N-oleoylsarcosine acid	$C_8C=CC_7CO-N(CH_3)CH_2CO_2H$	0.5	No	NT
3	dodecylsuccinic acid	$C_{12}-CH(CO_2H)CH_2CO_2H$	0.72	No	NT
4	ricinoleic acid	$C_8-CH(OH)-CH_2CH=CH-C_7CO_2H$	0.45	No	NT
5	lauric acid	$C_{11}CO_2H$	0.43	No	20+
6	tridecanoic acid	$C_{12}CO_2H$	0.45	No	NT
7	dodecylphosphoric acid	$C_{12}-O-PO(OH)_2$	0.45	No	NT
NT = Not Tested					



Without being limited, this invention encompasses a variety of compositions, uses and effective use options depending on the composition and use envisioned as is apparent from reading this specification and is not limited to any specific operation, composition or use but for example includes those operations such as whereby a  
5 composition is applied to, applied by, brought in contact with or effectively provided to by any effective application means including illustratively such as those known to those of skill in the art including for example deluge, pump, misting, spraying and the like to a metal or to a tool depending, of course, on use and composition. All parts and percentages employed herein are by weight unless otherwise specifically recited.

10 Although the invention has been described above in terms of some specific embodiments which are set forth in considerable detail, it should be understood that this description is by way of illustration only and that the invention is not necessarily limited thereto, since alternative embodiments and operating techniques will become apparent to those skilled in the art in view of this disclosure. Accordingly,  
15 modifications are contemplated which can be made without departing from the spirit of the aforescribed invention.

## WHAT IS CLAIMED IS:

1. A composition for metal working which comprises providing as a lubricant to said metal or tool working the metal or both, a lubricating functionally effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first group (A) comprising:  
amides; polyamides; amino acids, salts and esters; polyamino acids, salts and esters; monocarboxylic acids having one to six carbon atoms functionalized or nonfunctionalized, examples are  $C_1$  -  $C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or esters; keto acids, salts and esters; amine substituted organic acid(s) or a salt(s) thereof; sulfonic acids and salts, amino acids, salts and esters; a sulfur compound selected from mercaptan, sulfide, disulfide or polysulfide; mercaptocarboxylic acids, salts or esters; substituted amino acids, salts or esters; organosulfonates; sodium or potassium sulfide; sodium hydrogen or potassium hydrogen sulfide; organic acids containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate and phosphonate present as free acids or their salts, and additionally a moiety selected from the group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, carboxylic ester, ketone, amide, amine, ether, sulfide, disulfide, or

aryl; and optionally one or more components selected from a second Group (B) comprising:  
phosphates, borates, phosphonates, phosphites and hypophosphites, and  
which composition provides a synergistic lubricating or added functionality effect.

2. The composition of Claim 1 wherein said composition comprises a reaction product(s) of said composition associated with a component or components therein or the application of said composition to a metal being worked or tool working the metal or both.
3. The composition of Claims 1 or 2 wherein the lubricant has a lubricant property selected from the group consisting of extreme pressure, boundary lubricant, simple film or anti-wear or a combination thereof.
4. The composition of Claim 3 wherein said lubricant is an extreme pressure lubricant and said component of Group A is a monocarboxylic acid having one to six carbon atoms functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid with the proviso Group A does not include 2-hydroxybutyric or 3-hydroxybutyric acid.
5. The composition of Claim 3 wherein said lubricant is a boundary lubricant and said component of Group (A) has a chemical structure symbolically  $R_1COOH$

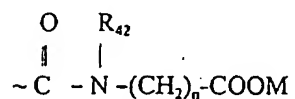
wherein  $R_1$  may be  $R_3OR_6$ , where  $R_3$  is  $C_{6-20}$  linear or branched alkyl, and  $R_6$  is  $C_{1-6}$  linear or branched alkylene or  $R_1$  may be  $R_7SR_4$  where  $R_7$  is  $C_{1-20}$  alkyl and  $R_4$  is  $C_{1-6}$  alkylene or hydroxyalkylene.

5. The composition of Claims 1 or 2 wherein said carboxylic acid contains two or more carboxylate moieties.
6. The composition of Claim 6 wherein said carboxylic acid is a polymer with repeating units which contain carboxylate groups.
7. The composition of claims 1 or 2 wherein said component of Group A is an amide or a polyamide in which the polyamide may be a molecule containing two or more amide groups or a polymer in which the repeating unit contains an amide group.
9. The composition of claim 6 wherein said polyamide is a polymer with repeating units which contain amide groups or wherein said amide or polyamide is a water soluble amide or water soluble polyamide respectively.
10. The composition of claim 9 where said amide is a compound or its salt and where the nitrogen may be substituted or unsubstituted, and which are represented by the formula:
 
$$R_7CONR_8R_9 \quad (V)$$

where  $R_7$ ,  $R_8$  and  $R_9$  as employed in formula (V) can be independently alkyl, functionalized alkyl, aryl, functionalized aryl, a functional group containing

alkyl or aryl groups,  $\text{NH}_2$ ,  $\text{NHR}_{10}$ , or  $\text{NR}_{11}\text{R}_{12}$ , where  $\text{R}_{10}$ ,  $\text{R}_{11}$  and  $\text{R}_{12}$  can be the same or different independently and can be hydrogen, alkyl, functionalized alkyl, aryl, or functionalized aryl groups with the provision that  $\text{R}_8$  and  $\text{R}_9$  may not be polyethyleneimine, when  $\text{R}_7$  is  $\text{MOOC}(\text{CH}_2)_8$ ,  $\text{R}_8$  and  $\text{R}_9$  may not be  $\text{C}_{1-4}$  hydroxyalkyl and when  $\text{R}_7$  is  $\text{C}_{12-18}$  alkyl,  $\text{R}_8$  and  $\text{R}_9$  may not be hydroxyethyl-. Furthermore, if one of  $\text{R}_8$  and  $\text{R}_9$  is hydrogen, and the other is  $\text{C}_{3-30}$  alkyl, then  $\text{C}_7$  may not be selected from  $-\text{CH}_2\text{CH}_2\text{COOH}$ ,  $-\text{CH}=\text{CHCOOH}$ , or ortho-carboxyphenyl and when one of  $\text{R}_8$  or  $\text{R}_9$  is H, and the other is  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , then  $\text{R}_7$  may not be an alkyl group containing from 8 to 22 carbon atoms.

11. The composition of claim 10 where said amide is



$n$  is an integer varying independently from two to ten

$\text{R}_{42} = \text{H}$  or alkyl  $\text{C}_1$  to  $\text{C}_{20}$

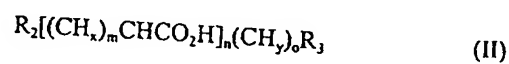
12. The composition of claim 9 wherein said amide is selected from the group consisting of asparagine, maleamic acid, urea, biuret, polyasparagine, glutamine, polyurea, N, N-dimethylacetamide, oleamide, guanidine, pyroglutamic, polyacrylamide, and poly(2-ethyl-2-oxazoline), a salt(s) and mixtures thereof.

13. A composition of claim 9 wherein said amide is selected from the group consisting of asparagine, maleamic acid, urca, polyasparagine, glutamine, pyroglutamic acid, polyacrylamide, and poly(2-ethyl-2-oxazoline) or a salt(s) thereof.

14. The composition of claims 1 or 2 wherein said component of Group A is a carboxylic acid as its acid or salt, which can be schematically represented by the formulas:



where in connection with formula (I),  $R_1$  is hydrogen,  $C_{1-6}$  alkyl, or  $R_1$  is  $R_2OR_3$ , where  $R_2$  is  $C_{6-20}$  linear or branched alkyl, and  $R_3$  is  $C_{1-6}$  linear or branched alkylene, or  $R_1$  may equal  $R_4SR_5$ , where  $R_4$  is  $C_{1-20}$  alkyl, and  $R_5$  is  $C_{1-6}$  alkylene or hydroxyalkylene, and

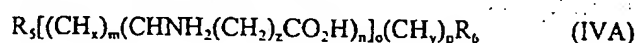
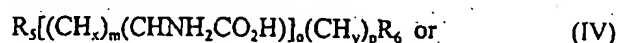


wherein connection with formula (II),  $R_2$  and  $R_3$  are the same or different independently and may be independently hydrogen or oxygen or an organic group including alkyl, and/or aryl, mercapto, thio or dithiorganic moieties, hydroxy, hydroxyalkyl, alkenyl, or alkoxy, alkoxyalkyl, or aromatic when employed in this formula (II),  $x$  and  $y$  are numerically either 1 or 2,  $m$  is 0 to about 40,  $o$  is 0 to about 18, and  $n$  is 1 to about 5000 or 7000 or more and  $m$ ,  $n$ , and  $o$  are independent integers with the proviso that  $R_1$  cannot be 3-carboxypropyl or 2-carboxymethyl substituted alkyl.

15. The composition of claim 13 wherein said carboxylic acid is selected from the group consisting of N-phosphonomethylglycine and water soluble salts

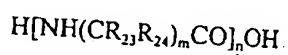
and esters; lactic acid, formic acid, glycolic acid, glyoxylic acid, glyceric acid, octylthiobutyric acid, octylthiopropionic acid, octyloxypropionic acid, decyloxypropionic acid, dodecyloxypropionic acid, 4-methylthio-2-hydroxybutyric acid, and salts and esters thereof and mixtures thereof.

16. The composition of claim 13 wherein said carboxylic acid is a polycarboxylic acid selected from the group consisting of polyacrylic acid, butanetetracarboxylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, dodecanedioic acid, undecanedioic acid, propanetricarboxylic acid, tartaric acid, sebacic acid, maleic acid, fumaric acid, citric acid, itaconic acid, citraconic acid, tartaric acid, malic acid, aconitic acid, and brassylic acid and tricarboxyhexane(s) and salts and esters thereof.
17. The composition of claims 1 or 2 wherein said component is an amino acid or a salt(s) thereof.
18. The composition of claim 16 wherein said amino acid is selected from amino acids which include both the naturally occurring amino acids and manufactured compounds containing at least one each of a carboxylic acid group and an amine group and are represented by the formulas:



Where  $R_4$ ,  $R_5$  and  $R_6$  in formulas (III) and (IV) are either the same or different independently and may be independently hydrogen, alkyl or aryl, carboxyl, carboxymethyl, hydroxyalkyl, or amine,  $x$ ,  $y$ , and  $z$  as employed in these formulas are the same or different independently and either 1 or 2,  $m$  and  $p$  as employed in these formulas are the same or different independently and can be 0 to 6 and  $r$  is an integer varying independently from 1 to 10. However,  $n$  and  $o$  must be at least one but can be integers from one to six independently, salts or esters thereof.

17. The composition of claim 17, where the component is methionine hydroxy analog or a salt(s) thereof.
18. The composition of claim 17 wherein the component of Group A is a polyamino acid or a salt(s) thereof.
19. The composition of claim 18 wherein the polyamino acid component is a homopolymer of an amino acid, a random or block copolymer of a single or two or more amino acids or a salt(s) thereof.
20. The composition of claim 19 wherein said polyamino acid component is prepared via synthesis or obtained from natural protein sources, both animal and vegetable, which are water soluble as either the free polymer or as a salt, and described by the following formula



(VIII)

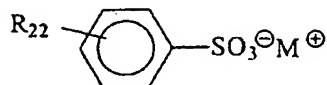


where m as employed in this formula (VIII) is an integer varying independently from 1 to 12, n is an integer independently varying from 2 to about 2000 or more and selected such that the amino acid remains water soluble,  $R_{23}$  and  $R_{24}$  as employed in this formula (VIII) can be the same or different independently and vary within one polymer chain and consist independently of hydrogen or  $-\text{CO}_2\text{H}$ ,  
 $-\text{CH}_2\text{CO}_2\text{H}$ ,  $-\text{CH}_2\text{CH}_2-\text{CO}_2\text{H}$ ,  $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_3$ ,  
 $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $\text{CH}(\text{CH}_3)_2$ ,  $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ ,  $-(\text{CH}_2)_o\text{X}$  where  $o = 0$  to 20 and X can be  $R_{23}$ ,  $-\text{OH}$ ,  $-\text{SH}$ ,  $-\text{SSCH}_2\text{CH}(\text{NH}_2)-$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{SCH}_3$ , phenyl, tolyl, hydroxyphenyl, guanidinyll, pyrrolidinyl,  $\text{NH}_2$ , imidazolyl, indolyl, acetoamide mixtures thereof and the like.

21. The composition of claim 20 wherein said polyaminoacid component is polyproline or a copolymer of proline with another amino acid or a salt(s) thereof.
22. The composition of claim 16 wherein said amino acid compound is an acidic amino acid or a salt(s) or mixture thereof.
23. The composition of claim 16 wherein said amino acid compound is a basic amino acid or a salt(s) or mixture thereof.
24. The composition of claim 18 wherein said amino acid compound is a neutral amino acids or mixture thereof.

25. The composition of claim 22 wherein said acidic amino acid is selected from the group consisting of aspartic acid and glutamic acid and isomers and racemic forms thereof and N, N-(2-carboxymethyl)N-methylphosphonic acid, N-phosphonomethylglycine, salt derivatives, and esters, O-phosphoserine and mixtures thereof.
26. The composition of claim 23 wherein said basic amino acid is selected from the group consisting of arginine, histidine, ornithine, and tryptophan and mixtures thereof.
27. The composition of claim 1 wherein said component is a sulfur containing amino acid.
28. The composition of claim 27 wherein said sulfur containing amino acid is selected from the group consisting of cysteine, cystine, methionine hydroxy analog, homocysteine, feline, penicillamine, methionine, isovalthine, vitamin-U and a salt(s) and mixture thereof.
29. The composition of claim 24 wherein said component is selected from amino acids including alanine, tyrosine, asparagine, valine, glutamine, glycine, hydroxyproline, isoleucine, leucine, phenylalanine, serine, threonine, thyroxine, norleucine, and norvaline.
30. The composition of claim 1 wherein said component of Group A is a sulfonate compound which is an organosulfonate.

31. The composition of claim 1 wherein said component of Group A is an:



(VII)

where  $R_{22}$  in formula (VII) is independently alkyl, alkoxy, hydrogen, aryl, aminoalkyl, amine, carboxyl, hydroxyl, or amide and M is independently hydrogen, alkali metal, ammonium, or organoammonium or mixtures thereof and the like.

32. The composition of claim 30 wherein said organosulfonate has an alkyl group which is substituted.
33. The composition of claim 30 where said organosulfonate is selected from the group consisting of 4-octylbenzenesulfonic acid, 2-octylbenzenesulfonic

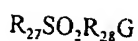
acid, 3-octylbenzenesulfonic acid, 4-nonylbenzenesulfonic acid, 2-nonylbenzenesulfonic acid, 3-nonylbenzenesulfonic acid, 4-decylbenzenesulfonic acid, 2-decylbenzenesulfonic acid, 3-

decylbenzenesulfonic acid, 4-undecylbenzenesulfonic acid, 2-undecylbenzenesulfonic acid, 3-undecylbenzenesulfonic acid, 4-dodecylbenzenesulfonic acid, 2-dodecylbenzenesulfonic acid, 3-dodecylbenzenesulfonic acid, and similar compounds containing different alkyl chain lengths, a salt(s) thereof and the like.

34. The composition of claim 33 wherein the organosulfonate is present as the alkali metal, ammonium or organoammonium salt or a mixture thereof.
35. The composition of claim 1 wherein the component of Group B is a phosphate.
36. The composition of claim 1 wherein the component of Group B is an orthophosphate.
37. The composition of claim 36 wherein said orthophosphate is selected from the group consisting of the monobasic, dibasic or tribasic salt or a salt or mixtures thereof having a cation selected from an alkali metal, potassium or sodium, or ammonium or alkylammonium.
38. The composition of claim 1 wherein the phosphonates are selected from the group consisting of those which can be represented by the formula:
- $$R_{25}(PO(OR_{26})_2)_n \quad (IX)$$
- where n in formula (IX) is an integer varying independently from 1 to about 5, and  $R_{25}$ , in formula (IX) can be independently organic moiety and

phosphonoorganic moiety(s), or amine containing organic moiety(s) or mixtures thereof and the like and  $R_{26}$  is independently hydrogen or an organic moiety(s) including alkyl, aryl, polyalkylene glycols, polypropylene glycols, mixtures thereof and the like.

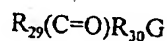
39. The composition of claim 38 wherein said phosphates, as their salts, are selected from the group consisting of pyrophosphoric acid, metaphosphoric acid, hypophosphoric acid, phosphorous acid, polyphosphoric acid and mixtures thereof.
40. The composition of claim 1 wherein the component of group B is a phosphonic acid or salt thereof.
41. The composition of claim 1 wherein the component of Group A is selected from 1-hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylenephosphonic acid), dodecylamine bismethylenephosphonic acid, which can be made by reacting dodecylamine, formaldehyde, phosphorous acid and hydrogen chloride, (hexamethylenediaminetetra(methylenephosphonic) acid, diethylenetriaminepenta(methylenephosphonic acid), N-phosphonomethylglycine, 2-phosphono-1,2,4-butanetricarboxylic acid, hydroxyphosphonoacetic acid, a salt or mixture thereof and the like.
42. The composition of claim 1 wherein the component of Group A is a sulfone acid of the formula:



(X)

where  $R_{27}$  is selected from linear or branched, substituted or unsubstituted, alkyl, alkenyl, alkoxyl, alkylamino groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and  $R_{28}$  is absent or selected from linear or branched, unsubstituted or substituted alkylene or alkenylene, alkoxyl, alkylamino groups containing 1 to 6 carbon atoms optionally containing one or more oxygen atoms and G is selected from  $CO_2M$ ,  $OSO_3M$ ,  $SO_2OM$ ,  $OPO(OM)_2$ , or  $PO(OM)_2$  where M is H, alkali metal cation, alkaline earth metal cation, ammonium and mixtures thereof.

43. The composition of Claim 42, wherein the component is octylsulfonylbutyric acid, octylsulfonylpropanoic acid, dodecylsulfonyl butyric acid, dodecylsulfonylpropanoic acid, N-octylsulfonyl-beta-alanine, nonylaminosulfonyl propanoic acid and a salt(s) or a mixture(s) thereof.
44. The composition of Claim 1, wherein the component of Group A is a keto acid of the formula:

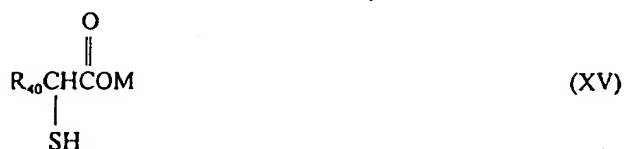


(XI)

where  $R_{29}$  is selected from hydrogen, linear or branched, substituted or unsubstituted, alkyl, alkenyl, alkoxyl groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and  $R_{30}$  is absent or selected from hydrogen, linear or branched, unsubstituted or substituted alkylene or alkenylene, alkoxyl groups containing 1 to 6 carbon atoms optionally containing one or more oxygen atoms and G is selected from  $CO_2M$ ,  $OSO_3M$ ,

SO<sub>2</sub>OM, OPO(OM)<sub>2</sub>, or PO(OM)<sub>2</sub> where M is hydrogen, alkali metal cation, alkaline earth metal cation, and ammonium and mixtures thereof.

45. The composition of claim 44, wherein the component of Group A is selected from the group consisting of monooctyl succinate, monododecylsuccinate, 5-oxo-hexadecanoic acid and a salt(s) or mixture(s) thereof.
46. The composition of Claim 1, wherein the component of Group A is a mercaptocarboxylic acids illustrated by the following schematic formula:



wherein R<sub>40</sub> includes alkyl C<sub>1-30</sub> and carboxyalkyl C<sub>1-30</sub>, x= 0 to 6, M=H, alkali metal, ammonium, mixtures thereof and the like.

47. The composition of Claim 1, wherein the component of Group A is an amine substituted organo acid of the formula:



where R<sub>31</sub> is selected from hydrogen, linear or branched, substituted or unsubstituted, alkyl, alkenyl, alkoxy groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and R<sub>32</sub> is absent or selected from hydrogen, linear or branched, unsubstituted or substituted alkylene or

alkenylene, alkoxyl, alkylamino groups containing 1 to 6 carbon atoms optionally containing one or more oxygen atoms and  $R_{33}$  is hydrogen or selected from linear or branched, substituted or unsubstituted, alkyl or alkenyl groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and G is selected from  $-\text{CO}_2\text{M}$ ,  $-\text{OSO}_3\text{M}$ ,  $-\text{SO}_2\text{OM}$ ,  $\text{OPO}(\text{OM})_2$ , or  $-\text{PO}(\text{OM})_2$  where M is H, alkali metal cation, alkaline earth metal cation, ammonium with the proviso that when G in the compound represented by the structure shown in formula (XII) is sulfonate, and  $R_{31}$  and  $R_{33}$  are not hydrogen.

48. The composition of Claim 1, wherein the component of Group A is a substituted amino acid(s) of the formula:



The compounds of formula (XIII) represent an extension of the amino acids wherein  $R_{34}$ ,  $R_{35}$ ,  $R_{36}$ , and  $R_{37}$  may be hydrogen, alkyl, aryl, functionalized alkyl, functionalized aryl, alkanol, polyalkoxy, alkenyl, sulfur containing moieties, and phosphorus containing moieties. Additionally,  $R_{34}$  and  $R_{36}$  may be covalently connected such as in cyclic amino acids like proline. M is conveniently a symbol for a moiety which is conveniently selected from hydrogen, an alkali metal, ammonium, or organoammonium, mixtures thereof and the like.



49. The composition of Claim 1, wherein the component of Group A is a substituted acid of the formula:



where  $R_{38}$  is selected from linear or branched, substituted or unsubstituted, alkyl or alkenyl groups having 6 to 20 carbon atoms optionally containing one or more oxygen atoms, and X is absent or selected from the group consisting of  $-CH_2-$  (methylene), oxygen, sulfur,  $-S-S-$ , and aryl where aryl is unsubstituted or substituted phenyl, and  $R_{39}$  is absent or selected from linear or branched, unsubstituted or substituted alkylene or alkenylene groups containing 1 to 6 carbon atoms, optionally one or more oxygen atoms, or  $(CH_2CH_2-O)_n$  where n can be 1 to 10, and G is selected from  $-OSO_2M$ ,  $-SO_2OM$ ,  $-OPO(OM)_2$ , or  $-PO(OM)_2$  where M is H, alkali metal cation, alkaline earth metal cation, or ammonium, with the proviso that:

1. when X is aryl and  $R_{39}$  is absent, G can not be  $SO_2OM$  and
2. when X is absent or methylene, G can not be  $PO(OM)_2$  and
3. when G is a phosphate then  $R_{38}$  cannot be substituted with phosphate and
4. when X is absent or methylene or oxygen, G cannot be phosphate and
5. when G is phosphate,  $R_{39}$  must be present and X cannot be methylene and
6. when is  $-SO_2OMg$  and X is absent or methylene then  $R_{38}$ ,  $R_{39}$  cannot be alkyl or alkylene. (Mg = magnesium.)

50. The composition of claim 1 wherein the component of group A is lactic acid or a salt(s) thereof and the component of group B is a phosphate.

51. The composition of claim 1 wherein the component of group A is lactic acid or a salt(s) thereof.
52. The composition of claim 1 wherein the component of group A is polyacrylic acid or a salt(s) thereof and the component of group B is a phosphate.
53. The composition of claim 1 wherein the component of group A is aspartic acid or a salt(s) thereof and the component of group B is a phosphate.
54. The composition of claim 1 wherein the component of group A is aspartic acid or a salt(s) thereof.
55. The composition of claim 1 wherein the component of group A is glutamic acid or a salt(s) thereof and the component of group B is a phosphate.
56. The composition of claim 1 wherein the component of group A is glutamic acid or a salt(s) thereof.
57. The composition of claim 1 wherein the component of group A is polyglutamic acid or a salt(s) thereof and the component of group B is a phosphate.
58. The composition of claim 1 wherein the component of group A is polyglutamic acid or a salt(s) thereof.

59. The composition of claim 1 wherein the component of group A is polyasparagine and the component of group B is a phosphate.
60. The composition of claim 1 wherein the component of group A is polyasparagine.
61. The composition of Claim 1, wherein the component of Group A is polyaspartic acid or a salt(s) thereof and the component of Group B is phosphate.
62. The composition of claim 1 wherein the component of group A is polyaspartic acid or a salt(s) thereof.
63. The composition of Claim 1, wherein the component of Group A is aspartic or a salt(s) thereof and the component of Group B is phosphate.
64. The composition of Claim 1, wherein the component of Group A is polyaspartic or a salt(s) thereof and the component of Group B is borate.
65. The composition of Claim 1, wherein the component of Group A is aspartic or a salt(s) thereof and the component of Group B is borate.
66. The composition of claim 1 wherein the component of group A is urea and the component of group B is a phosphate.

67. The composition of claim 1 wherein the component of group A is dithiodipropionic acid or a salt(s) thereof and the component of group B is a phosphate.
68. The composition of claim 1 wherein the component of group A is N-phosphonomethylglycine or a salt(s) thereof and the component of group B is a phosphate.
69. The composition of claim 1 wherein the component of group A is N-phosphonomethylglycine or a salt(s) thereof.
70. The composition of claim 1 wherein the component of Group A is of glycerol-2-phosphate and the component of Group B is a phosphate.
71. The composition of claim 1 wherein the component of Group A is 1,3-dihydroxyacetone dimer and the component of Group B is a phosphate.
72. The composition of claim 1 wherein the component of Group A is 2,4,6-trichlorophenol and the component of Group B is a phosphate.
73. The composition of claim 1 wherein the component of Group A is polyaspartate and the component of Group B is 1-hydroxyethylidene-1, 1-diphosphonic acid or a salt(s) thereof.

74. The composition of claim 1 wherein the component is polyacrylic acid or a salt(s) thereof.
75. The composition of claim 1 wherein the component of Group A is tricarboxyhexane or a salt(s) thereof.
76. The composition of claim 1 wherein the component of Group A is 1,2,3,4-butanetetracarboxylic acid or a salt(s) thereof.
77. The composition of claim 1 wherein the component of Group A is cystine or a salt(s) thereof.
78. The composition of claim 1 wherein the component of Group A is sodium sulfide.
79. The composition of claim 1 wherein the component of Group A is cysteine or a salt(s) thereof.
80. The composition of claim 1 wherein the component of Group A is 1-hydroxyethylidene-1, 1-diphosphonic acid or a salt(s) thereof.
81. The composition of claim 1 wherein the phosphorus moiety from Group B is provided by dodecylamino bismethylene phosphonate or a salt(s) thereof.

82. The composition of claim 1 wherein the component of Group A is dodecylaminebis(methylene phosphonic acid) or a salt(s) thereof.
83. The composition of Claim 1 wherein the component of Group A is tartaric acid or a salt(s) thereof and the component of Group B is phosphate.
84. The composition of Claim 1 wherein the component of Group A is malic acid or a salt(s) thereof and the component of Group B is phosphate.
85. The composition of claim 1 wherein the component of group A is malic acid or a salt(s) thereof.
86. The composition of Claim 1 wherein the component of Group A is citric acid or a salt(s) thereof and the component of Group B is phosphate.
87. The composition of claim 1 wherein the component of Group A is citric acid or a salt(s) thereof.
88. The composition of Claim 1 wherein the component of Group A is oxalic acid or a salt(s) thereof and the component of Group B is phosphate.
89. The composition of claim 1 wherein the component of Group A is oxalic acid or a salt(s) thereof.

90. The composition of Claim 1 wherein the component of Group A is 1,2,3,4-butanetetracarboxylic acid or a salt(s) thereof and the component of group B is phosphate.
91. The composition of Claim 1 wherein the component of Group A is 1,3,6-tricarboxyhexane acid or a salt(s) thereof and the component of Group B is phosphate.
92. The composition of claim 1 wherein the component of group A is 1,3,6-tricarboxyhexane acid or a salt(s) thereof.
93. The composition of Claim 1 wherein the component of Group A is polyacrylic acid or a salt(s) thereof and the component of Group B is phosphate.
94. The composition of Claim 1 wherein the component of Group A is 2-phosphono-1,2,4-butanetricarboxylic acid or a salt(s) thereof.
95. The composition of Claim 1 wherein the component of Group A is aspartic acid or a salt(s) thereof and the component of Group B is phosphate.
96. The composition of Claim 1 wherein the component of Group A is L-glutamic acid or a salt(s) thereof and the component of Group B is phosphate.

97. The composition of Claim 1 wherein the component of Group A is N-cocoylglutamate or a salt(s) thereof and the component of Group B is phosphate.
98. The composition of Claim 1 wherein the component of Group A is ornithine or a salt(s) thereof and the component of Group B is phosphate.
99. The composition of Claim 1 wherein the component of Group A is arginine or a salt(s) thereof and the component of Group B is phosphate.
100. The composition of Claim 1 wherein the component of Group A is L-asparagine or a salt(s) thereof and the component of Group B is phosphate.
101. The composition of Claim 1 wherein the component of Group A is L-glutamine or a salt(s) thereof and the component of Group B is phosphate.
102. The composition of claim 1 wherein the component of Group A is phenylalanine or a salt(s) thereof.
103. The composition of claim 1 wherein the component of Group A is glycine or a salt(s) thereof and the component of Group B is phosphate.
104. The composition of claim 1 wherein the component of Group A is glycine or a salt(s) thereof.



105. The composition of Claim 1 wherein the component of Group A is the alkali or ammonium salt of polyglutamic acid and the component of Group B is phosphate.
106. The composition of Claim 1 wherein the component of Group A is polyaspartate and the component of Group B is phosphate.
107. The composition of Claim 1 wherein the component of Group A is polyasparagine and the component of Group B is phosphate.
108. The composition of Claim 1 wherein the component of Group A is polyaspartate and the component of Group B is 1-hydroxyethylidene-1,1-diphosphonic acid or a salt(s) thereof.
109. The composition of claim 1 wherein the component of Group A is 1-hydroxyethylidene-1, 1-diphosphonic acid or a salt(s) thereof.
110. The composition of Claim 1 wherein the component of Group A is bovine somatotropin hormone and the component of Group B is phosphate.
111. The composition of Claim 1 wherein the component of Group A is urea and the component of Group B is phosphate.
112. The composition of Claim 1 wherein the component of Group A is polyacrylamide and the component of Group B is phosphate.

113. The composition of Claim 1 wherein the component of Group A is polyacrylamide.
114. The composition of claim 1 wherein the component of Group A is poly(2-ethyl-2-oxazoline).
115. The composition of Claim 1 wherein the component of Group A is poly(2-ethyl-2-oxazoline) and the component of Group B is phosphate.
116. The composition of claim 1 wherein the component of Group A is lysine or a salt(s) thereof and the component of Group B is borate.
117. The composition of Claim 1 wherein the component of Group A is succinamic acid or a salt(s) thereof and the component of Group B is phosphate.
118. The composition of Claim 1 wherein the component of Group A is succinamic acid or a salt(s) thereof.
119. The composition of Claim 1 wherein the component of Group A is maleamic acid or a salt(s) thereof and the component of Group B is phosphate.
120. The composition of Claim 1 wherein the component of Group A is maleamic acid or a salt(s) thereof.

121. The composition of Claim 1 wherein the component of Group A is pyroglutamic acid or a salt(s) thereof and the component of Group B is phosphate.
122. The composition of Claim 1 wherein the component of Group A is pyroglutamic acid or a salt(s) thereof.
123. The composition of claim 1 wherein the component of Group A is N-phosphonomethylglycine or a salt(s) thereof.
124. The composition of Claim 1 wherein the component of Group A is N-phosphonomethylglycine or a salt(s) thereof and the component of Group B is phosphate.
125. The composition of Claim 1 wherein the component of Group A is N, N-di(2-carboxymethyl)-N-methylphosphonic acid or a salt(s) thereof.
126. The composition of Claim 1 wherein the component of Group A is O-phosphoserine or a salt(s) thereof.
127. The composition of Claim 1 wherein the components of Group A are L-glutamic or a salt(s) thereof and borate.

128. The composition of Claim 1 wherein the components of Group A are polyaspartate and polyacrylate.
129. The composition of Claim 1 wherein the component of Group A is potassium polyacrylate.
130. The composition of claim 1 wherein the components of Group A are potassium polyaspartic acid and polyacrylate and the component of Group B is phosphate.
131. The composition of Claim 1 wherein the component of Group A is polyacrylamide and the component of Group B is phosphate.
132. The composition of Claim 1 wherein the component of Group A is polyacrylamide.
133. The composition of claim 1 wherein the component of Group A is a formic acid salt.
134. The composition of Claim 1 wherein the component of Group A is formic acid or a salt(s) thereof and the component of Group B is phosphate.
135. The composition of claim 1 wherein the component of Group A is 4-hydroxybutyric acid or a salt(s) thereof.

136. The composition of claim 1 wherein the component of Group A is 4-hydroxybutyric acid or a salt(s) thereof and the component from Group B is phosphate.
137. The composition of Claim 1 wherein the component of Group A is bovine serum albumin and the component of Group B is phosphate.
138. The composition of Claim 1 wherein the component of Group A is 2-mercapto succinic acid or a salt(s) thereof and component of Group B is phosphate.
139. The composition of claim 1, wherein said component of Group B is  $K_2 B_{10} O_{16}$ .
140. The composition of claim 1, wherein said component of Group B is  $K_2 B_{10} O_{16}$  and said component of Group A is polyaspartic acid.
141. The composition of claim 1, wherein said component of Group A is poly(2-ethyl-2-oxazoline) and said component of Group B is a borate.
142. The composition of claim 1, wherein said component of Group A is L-glutamic acid or a salt(s) thereof and said component of Group B is a borate.
143. The composition of claim 1, wherein said component of Group A is L-aspartic or a salt(s) thereof and said component of Group B is a borate.

144. The composition of claim 1, wherein said component of Group A is citric acid or a salt(s) thereof and said component of group B is a borate.
145. The composition of claim 1, wherein said component of Group A is malic acid or a salt(s) thereof and said component of Group B is a borate.
146. The composition of claim 1, wherein said component of Group A is urea and said component of Group B is a borate.
147. The composition of claim 1, wherein said component of Group B is boric acid or a salt(s) thereof and said component of Group A is polyaspartate.
148. The composition of claim 1, wherein said component of Group B is boric acid or a salt(s) thereof.
149. The composition of claim 1, wherein said component of Group A is dithiodipropionic acid or a salt(s) thereof.
150. A method for metal working, wherein said method comprises providing as a lubricant to said metal, a lubricating effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbons functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$  alkoxy, sulfone, alkylcne phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters, sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide; and mercaptocarboxylic acids, salts and esters; amine substituted organic acids, salts and esters; substituted amino acids, salts or esters; organosulfonates; sodium or potassium sulfide, sodium or potassium hydrogen sulfide, organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate; and phosphonate present as the free acids or their salts; and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising: phosphates, borates, phosphonates, phosphites and hypophosphites, and

which composition provides a synergistic lubricating or added functionality effect when used with one or more component(s) of Group (A) and Group (B).

151. The composition of claim 1 wherein the component of Group A is N-phosphonomethylglycine and its water soluble salts, esters and mixtures thereof.
152. The composition of claim 108 wherein the component is phosphonobutanetricarboxylic acid or a salt(s) thereof.
153. A composition of claim 1 wherein the component of Group A is a protein.
154. A composition of claim 154, wherein said protein is a naturally occurring protein.
155. A composition of claim 155, wherein said naturally occurring protein is selected from the Group consisting of bovine serum albumin, bovine somatotropin, gelatin, or casein.
156. The composition of claim 1 wherein the amount of a component selected from Group A is in the range from about 0.1% to about 75% by weight of the total composition.
157. The composition of claim 1 wherein the concentration of the component of Group A is in the range from about 0.25% to about 25% by weight for the total composition.



158. The composition of claim 1 wherein when a component is utilized from Group A and a component from Group B, the amount of a component selected from Group B is in the range from about 0.1 to about 60% by weight.
159. The preferred composition of claim 1 wherein the concentration of the component of Group B is preferably in the range from about 0.25 to about 15% by weight for the total composition.
160. The fluid composition of claim 1 wherein more than one component is utilized from Group A and/or from Group B.
161. The fluid composition of claim 1 wherein a phosphonate is selected as the component from Group B and the concentration of the phosphonate is in the range from about 0.075% to about 50%.
162. The composition of claim 1 wherein the preferred concentration of the phosphonate is in the range from about 0.10% to about 15% by weight composition.
163. The composition of claim 1 wherein the concentration of the phosphonate is in the range from about 0.10% to about 10% by weight.
163. A method of metal working of claim 1 wherein said metal working includes grinding and forming.

164. A method of metal working of claim 163 wherein said metal working is forming.
165. A method of metal working of claim 163 wherein said metal working is grinding.
166. A method of feeding a metal working water-soluble lubricant composition to a metal useful to receive the same, comprising optionally diluting said metal working water soluble lubricant composition and feeding the optionally diluted or non-diluted water soluble composition to a portion of the metal by applying (spraying or dripping) whereby said composition is effectively provided to said metal.
167. The method of claim 166 wherein said metal working water soluble lubricant composition is that which comprises providing as a lubricant to said metal, a lubricating effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:
- amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbon atoms functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters; sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and

polysulfide and 2 mercaptocarboxylic acid; keto acids, salts and esters; amine substituted organic acid(s) or a salt(s) thereof; organosulfonates; sodium or potassium sulfide, sodium or potassium hydrogen sulfide, organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate present as the free acids or their salts, and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising: phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used with one or more component(s) of Group (A) and Group (B).

168. A method for metal working, wherein said method comprises providing as a lubricant to said metal, a lubricating effective amount of a lubricant composition comprising of one or more water soluble components selected from: a first Group (A) comprising:

amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbons functionalized or nonfunctionalized, examples are

$C_1 - C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters, sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide; and mercaptocarboxylic acids, keto acids, salts and esters; amine substituted organic acid(s) or a salt(s) thereof; organosulfonates; sodium sulfide, sodium hydrogen sulfide, organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate; and phosphonate present as the free acids or their salts; and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising: phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used with one or more component(s) of Group (A) and Group (B).

169. The method of claim 166 wherein said metal working water soluble lubricant composition is that of claim 3.

170. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 4.
171. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 5.
172. The method of claim 168 wherein said metal working water soluble lubricant composition is that of claim 6.
173. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 7.
174. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 8.
175. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 9.
176. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 11.
177. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 12.

178. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 13.
179. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claim 14.
180. The method of claim 167 wherein said metal working water soluble lubricant composition is that of claims 14-149.
181. A lubricated metal surface wherein said surface of said metal being worked has been contacted with a composition comprising an effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:
- amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbon atoms functionalized or nonfunctionalized, examples are  $C_1 - C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters; sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide; organosulfonates; sodium sulfide, sodium hydrogen sulfide, organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; keto acids, salts and esters; amine

substituted organic acid(s) or a salt(s) thereof; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate; and phosphonate present as the free acids or their salts; and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, ketone, carboxylic ester, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising: phosphates, borates, phosphonates, phosphites and hypophosphites, and which composition provides a synergistic lubricating or added functionality effect when used with one or more component(s) of Group (A) and Group (B) lubrication has been provided.

182. The lubricated metal surface of claim 179 wherein said surface of said metal being worked has been lubricated with a composition of claim 2.
183. The lubricated metal surface of claim 179 wherein said surface of said metal being worked has been lubricated with a composition of claim 1.
184. The lubricated metal surface of claim 179 wherein said surface of said metal being worked has been cleaned first and subsequently lubricated with a composition of claim 1.
185. A method of claim 1 in which additional components are added to provide or enhance corrosion protection to the workpiece or equipment.

186. A method of claim 144, in which the corrosion inhibitors are longer chain and substituted mono- di- and tri-amines such as 2,2'-ethylenedioxy-bis(ethylamine), trioctylamine, tris (2-aminoethyl)amine, polyethyleneimine, and N,N,N',N'-tetrakis(2hydroxyethyl) ethylene diamine, 4(aminomethyl)-1, 8-octane diamine, iminobispropylamine, bishexamethylene-triamine.
187. A method of claim 145 in which the corrosion inhibitors are basic amino acids such as lysine or ornithine.
188. A method of claim 146 in which the corrosion inhibitors are biological buffers DIPSO (3-[N,N-bis(2-hydroxyethyl(amino))-2-hydroxy-propanesulfonic acid which are non-toxic and biodegradable.
189. A method of claim 1 in which corrosion inhibitors are imidazoles such as 1-methylimidazole, 1-(3-aminopropyl) imidazole, and 1,2 dimethylimidazole and the like.
190. An article of manufacture which comprises a worked piece of metal or a piece of metal being worked, said working being or having been accomplished by having contacted or provided to said metal with an effective amount of a fluid lubricant composition comprising one or more water soluble components selected from: a first Group (A) comprising:



amides; polyamides; polyamino acids, salts and esters; monocarboxylic acid having one to six carbons functionalized or nonfunctionalized, examples are  $C_1$ - $C_{20}$  alkoxy, sulfone, alkylene phosphonates, sulfide, functionalized amines and the like, salts and esters, with the proviso that this does not include the 2-hydroxybutyric acid and 3-hydroxybutyric acid; polycarboxylic acids, salts or their esters; amino acids, salts and esters; sulfonic acids and salts; a sulfur compound selected from mercaptan, sulfide, disulfide and polysulfide and mercaptocarboxylic acids, salts and esters; substituted amino acids, salts or esters; organosulfonates; sodium or potassium sulfide, sodium or potassium hydrogen sulfide, keto acids, salts and esters; amine substituted organic acid(s) or a salt(s) thereof, organic acid(s) containing one or more moieties selected from the group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate, present as the free acids, or their salts; organic acids containing one or more moieties selected from the Group consisting of carboxylate, sulfate, sulfonate, phosphate, and phosphonate present as the free acids or their salt, and additionally a moiety selected from the Group consisting of sulfone, sulfonamide, sulfonic ester, sulfate ester, carboxylic ester, ketone, amide, amine, ether, sulfide, disulfide, or aryl; and optionally one or more components selected from a second Group (B) comprising:

phosphates, borates, phosphonates, phosphites and hypophosphites, and

which composition provides a synergistic lubricating or added functionality effect when used in an admixture with one or more component(s) of Group (A) and Group (B) to produce said article of manufacture.

191. An article of manufacture of claim 1 wherein said composition is the composition of claim 2.
192. The article of manufacture of claim 188 wherein said composition is the composition of claim 3.
193. The article of manufacture of claim 188 wherein said composition is the composition of claim 4.
194. The article of manufacture of claim 188 wherein said composition is the composition of claim 5.
195. The article of manufacture of claim 188 wherein said composition is the composition of claim 6.
196. The article of manufacture of claim 153 wherein said composition is the composition of claim 7.
197. The article of manufacture of claim 154 wherein said composition is the composition of claim 8.
198. The article of manufacture of claim 155 wherein said composition is the composition of claim 9.

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207. The article of manufacture of claim 4 wherein said composition is the composition of claims 4-149.
208. A method of metal working wherein said metal working comprises all metal working operations including metal forming and/or grinding and/or metal removal using a composition of claim 1.
209. The composition of Claim 1, wherein the component of Group A is succinic acid or a salt(s) thereof.
210. The composition of Claim 1, wherein the component of Group A is succinic acid or a salt(s) thereof and the component of Group B is a phosphate.
211. The composition of claim 1, wherein the component of Group A is L-aspartyl-L-phenylalanine or a salt(s) thereof.
212. The composition of claim 1, wherein the component of Group A is L-aspartyl-L-phenylalanine, methyl ester or a salt(s) thereof.
213. The composition of claim 1, wherein the component of Group B is phosphate.
214. The composition of claim 1, wherein the component of Group B is phosphate.